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Method development for the quantification of radionuclide retention in repository-relevant construction and backfill materials

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Abstract

The final disposal of high-level radioactive waste (HLW) is one of the most difficult challenges of our time. In Germany, clay formations in northern Germany (model NORD) are considered as promising repository sites. To contribute to the safety assessment, this study investigated the retention of repository-relevant elements in/on important construction and backfill materials, in particular the cement (alteration) phase calcium silicate hydrate (C-S-H). Therefore, a study on the retention kinetics of Cs(I), Eu(III), Sm(III) and U(VI) in C-S-H phases was conducted. However, the overarching goal was to develop new analytical methods for quantifying important retention parameters. To this end, novel miniaturised column experiments (MCE) were developed. Using modern high-performance liquid chromatography (HPLC), these MCE enabled the successful performance of extremely resource- and time-efficient dynamic sorption and leaching experiments (remobilisation studies) under highly controllable conditions. This method was used, for example, to investigate the Cs(I) retention behaviour and the U(VI) remobilisation from C-S-H phases. In addition, an LA-ICP-MS (Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry) method was established for quantifying element ratios and trace elements in C-S-H phases. In summary, the work in this dissertation makes an important contribution to final repository research and to the safety case for a German final repository.

Kurzzusammenfassung

Die Endlagerung hochradioaktiver Abfälle (HLW) ist eine der schwierigsten Herausforderungen unserer Zeit. Für Deutschland gelten dabei norddeutsche Tongesteinsformationen (Modell NORD) als vielversprechende Endlagerungsstätte. Um zum Sicherheitsnachweis beizutragen, wurde in dieser Arbeit der Rückhalt endlagerrelevanter Elemente an wichtigen Bau- und Verfüllmaterialien, insbesondere der Zement(alterations-)phase Calcium-Silikat-Hydrat (C-S-H), untersucht. Hierzu wurde auch eine Studie zur Retentionskinetik von Cs(I), Eu(III), Sm(III) und U(VI) an C-S-H Phasen durchgeführt. Das übergeordnete Ziel war aber die Entwicklung neuer analytischer Methoden zur Quantifizierung wichtiger Retentionsparameter. Hierzu wurden neuartige miniaturisierte Säulenexperimente (MCE) entwickelt. Diese ermöglichten unter Verwendung moderner Hochleistungsflüssigchromatographie (HPLC) die Durchführung Ressourcen- und Zeit-sparender dynamischer Sorptions- und Leachingexperimente (Remobilisierungsstudien) unter kontrollierbaren Bedingungen. Mit dieser Methode wurde beispielsweise das Cs(I)-Retentionsverhalten an aber auch die U(VI)-Remobilisierung aus C-S-H Phasen untersucht. Zudem wurde eine LA-ICP-MS (Laserablation – Induktiv gekoppeltes Plasma – Massenspektrometrie) Methode zur Quantifizierung von Spurenelementen und Elementverhältnissen in C-S-H Phasen etabliert. Zusammenfassend leistet diese Arbeit einen wichtigen Beitrag zur Endlagerforschung und zum Sicherheitsnachweis für ein deutsches Endlager.

Abbreviations and symbols

λ	Wavelength	FACP	Frontal Analysis by Characteristic Point
Δ	Deviation in [%]	FBCE	Fixed bed column experiments
BTC	Break through curve	FEP	Features, Events, and Processes
C	Concentration	GC	Gas chromatography
C/S	Molar calcium to silicon ratio	HLW	High-level nuclear waste
C₂(F,A)₅	Calcium aluminoferrite	HPLC	High performance liquid chromatography
C₂S	Dicalcium silicate	I	Intensity
C₃A	Tricalcium aluminate	IAEA	International Atomic Energy Agency
C₃S	Tricalcium silicate	ICP-MS	Inductively coupled plasma mass spectrometry
C₀	Initial concentration	ICP-OES	Inductively coupled plasma emission spectroscopy
C_{eq}	Equilibrium concentration	ICP-QMS	Single quadrupole ICP-MS
CM-II	Colloidal Model II	ICP-QQQ	Tripple quadrupole ICP-MS
CPS	Counts per second	ID	Inner diameter
CRC	Collision/Reaction Cell	ILW	Intermediate-level radioactive waste
CRM	Certified reference materials	IM	Inverse method
CRZ	Containment providing rock zone	IS	Internal standard
C-S-H	Calcium silicate hydrate	K_F	Freundlich constant
DAD	Diode array detector	K_{HE}	Henry constant
DGS	Diluted gypsum solution	K_L	Langmuir constant
ECP	Elution by Characteristic Point	K_{TH}	Thomas constant
EDX	Energy dispersive X-ray spectroscopy	L	Length
EDZ	Excavation damaged zones	LA	Laser ablation
EW	Exempt waste	LC	Liquid chromatography
FA	Frontal analysis	LLW	Low-level radioactive waste
FAA	Flame atomic absorption	m	Mass

Abbreviations and symbols

$\dot{m}$	Mass flow rate	t	Ton (1,000 kg)
m/z	Mass to charge ratio	TLC	Thin-layer chromatography
MCE	Mini column experiments	V	Volume
MTZ	Mass transfer zone	VLLW	Very low-level radioactive waste
		VSLW	Very short-lived waste
n_F	Freundlich exponent	XRF/RFA	X-ray fluorescence spectroscopy
NIST®	National Institute of Standards and Technology		
NORM	Naturally occurring radioactive material		
NP	Normal phase chromatography		
ORS	Octopole Reaction System		
PBM	Planetary ball mill		
PM	Perturbation Method		
ppm	Parts per million		
ppq	Parts per quadrillion		
ppt	Parts per trillion		
q	Loading on adsorbent		
Q	Flow rate		
$q_{\max}$	Maximum Loading capacity		
R&D	Research and development		
R^2	Correlation coefficient		
R_d	Retention distribution ratio		
RF	Radio Frequency		
RI	Refractometer		
RM	Reference material		
RP	Reversed phase chromatography		
RSD	Relative Standard deviation		
S	Slope/Sensitivity		
S/L	Solid to liquid ratio [g L ⁻¹]		
SAM	Standard addition method		
SRM®	Standard Reference Material®		

1. Introduction and Motivation

The discovery of radioactivity led to the development of numerous technologies to utilise radioactive (decay) processes. For example, as of December 2025, 403 nuclear power plants are in operation worldwide, with another 34 closed for the long term and 223 closed permanently [1]. However, all nuclear technologies brought with them one of the most significant and important tasks of our time: the disposal of the highly radioactive nuclear waste (HLW) in a safe, economical, and environmentally sustainable manner. In this context, there is international consensus that HLW – originating primarily from spent fuel elements from nuclear power plants, waste from the reprocessing of these fuel elements, and material from decommissioned nuclear weapons - should be disposed of in deep geological formations [2-9].

In Germany, the host rocks rock salt, clay- and crystalline rock are generally considered for a potential HLW repository. Storage is planned in these geological host rock formations at depths of 300 - 1500 m using natural and artificial barriers. In the case of a repository in clay rock (e.g. location site model “NORD”), such a multi-barrier system consists of the HWL-Castor containers, cement-based materials used as construction, closure and/or backfill material, further backfill in and around the repository area (e.g. clay-based materials) and the geological host rock strata [2-5, 7, 10-12].

With that, cement-based materials are a crucial component in a variety of repository concepts – including the location site model “NORD”. But thinking about repositories in deep geological formations, the penetration/migration of porewater into the near field of the disposal site must be considered [3, 4, 13-15]. Unfortunately, in contact with penetrating pore water hydrated cement is not thermodynamically stable and corrodes over time, resulting in cement aging phases. Regarding the cement (aging-) phases, calcium silicate hydrate (C-S-H) phases are an essential component of both and are considered to be responsible for the heavy metal binding ability, making them a crucial component for a repository safety assessment [13, 16-19]. C-S-H Phases are described as cement-gel, which is mostly amorphous, but also contains domains with a semi-crystalline structure. The structure type of those domains mainly depends on the synthesis routine: 11 Å tobermorite, 14 Å tobermorite, jennite and xonolite are reported [13, 20-22]. C-S-H Phases are also not stable in contact with aqueous media and degrade over time, involving dissolution and precipitation processes. During this degradation the pH of the resulting alkaline porewater and the calcium to silicon (C/S) ratio correlate with each other [13, 22-25].

To effectively provide a safety assessment for a potential repository it is of immense interest to determine the extent to which radionuclides interact with the surrounding construction and backfill materials in the near field of the disposal site. Till this end numerous studies have been made regarding the investigation of the interaction of repository-relevant elements with the construction and backfill materials (see e.g. [8] and references therein), but it is virtually impossible to represent all potentially migrating elements in a single experiment or study. Therefore, a selection must be made: To contribute to a safety assessment, in this work the retention and remobilisation of the repository-relevant elements Mo(VI), Cs(I), Sm(III), Eu(III), and U(VI) on (mainly) C-S-H phases were investigated.

Thinking of the inventory of a repository, the first element that intuitively comes to mind is uranium. ^{235}U , more precisely UO_2 , is the main part of nuclear reactor fuel and therefore the most important radionuclide in the inventory [26-29]. Under repository-relevant conditions uranium is proposed to be present in the oxidation states +IV and +VI, with U(VI) predominating in a C-S-H environment [30-34]. In general, the retention of U(VI) on C-S-H, and to a small extent also the remobilisation from those, has already been studied in detail. It has been shown that the high U(VI) retention on cementitious materials (and C-S-H phases) is primarily due to precipitation, incorporation, direct surface complexation or a ternary Ca(II) uranate-like (surface) precipitates [19, 31, 34-43]. In this context the competition between Ca^{2+} and UO_2^{2+} and, especially in alkaline pH-ranges, the Ca^{2+} mediated U(VI) retention mechanism is postulated [30, 34, 39-42].

Although europium, itself, as $^{150\text{m}}\text{Eu}$, ^{152}Eu and ^{154}Eu , is mentioned by the International Atomic Energy Agency (IAEA) as one of the relevant radionuclides regarding the decommissioning/dismantling of nuclear facilities [44], in repository research it is mainly used for another reason. Lanthanides (e.g. Sm(III) and Eu(III)) have similar ionic radii to Am(III) and Cm(III) and are considered to behave similar in solution. Because of these chemical similarities, Eu(III) is often used as a less toxic and non-radioactive homologue [34, 45-49]. Similar to U(VI), the retention mechanism of Eu(III) on C-S-H phases has also been investigated in detail. In general, three different mechanisms are assumed here: incorporation into the C-S-H structure through substitution of Ca(II), formation of hydroxide surface complexes, and surface precipitates. In the latter case, Si-Ca-Eu(III) secondary phases are assumed in some places, which can also accumulate/adsorb on the C-S-H surface [16, 19, 34, 47, 50-53].

Although caesium occurs in nature only as the non-radioactive mononuclidic element ^{133}Cs , the artificially produced ^{137}Cs isotope, as a fission product in nuclear reactors, is very important for a safety assessment [2, 29, 54, 55]. Under repository-relevant conditions (in a cementitious/C-S-H environment) the only species reported is Cs^+ , which is furthermore postulated to not precipitate [12, 34, 56, 57]. It can therefore be concluded that the retention is solely due to adsorption. In the context of C-S-H phases three different sorption sites are reported: ion exchange reactions, inner and outer sphere complexes [34, 58-63].

The origin of molybdenum in a HLW repository inventory is often attributed to neutron capture reaction of different alloys in the near field of the reactor, whereas Mo can also be part of the nuclear fuel itself. In both cases the isotope of interest is ^{93}Mo [64-69]. Regarding the expected speciation of Mo in a cementitious/C-S-H environment, the statement is as simple as for Cs(I). It can be assumed that at a $\text{pH} > 8$, only Mo(VI) is present as MoO_4^{2-} [13, 70]. As for the other elements, C-S-H phases contribute significantly to the total retention of Mo(VI) in cementitious materials. Thereby the retention on C-S-H can be broken down to two mechanism: the electrostatic sorption on the positive C-S-H surface and the precipitation of powellite (CaMoO_4) [19, 71-74].

Although the retention mechanism of the elements described has already been investigated comprehensively, there are still important gaps to close. This work is now intended to address those gaps. While doing so, one big focus lies on the development of new and adapting/improving existing analytical methods to investigate the immobilisation and remobilisation behaviour of repository-relevant elements on also relevant construction and backfill materials in a more efficient and precise manner.

When evaluating the retention of repository-relevant elements on adsorption materials, the competition between those is often neglected. Furthermore, depending on the repository model and the disposal site, also the presence of high ionic strength porewaters must be considered, but retention studies under such conditions are still scarce. In a first published study those gaps were addressed: the retention kinetics Cs(I), Sm(III), Eu(III) and U(VI) on C-S-H phases was investigated in standardised batch experiments. Thereby the influence of two ionic strengths ($I = 0.1\text{ M}$ and 2.6 M) were investigated, and more importantly, those analytes were added in a mixture of 8 repository-relevant elements (Waste Cocktail) in total [34] (and references therein).

To investigate the retention behaviour and with that evaluating the adsorption capacity of different materials, not only in repository research, it is common practice to conduct standardised batch experiments. The greatest advantage of those is the high experimental throughput. However, due to the unrealistic solid-liquid (S/L) ratio and static equilibrium, batch experiments can only be considered a rough approximation of realistic conditions. Alternatively, column experiments are also known from the literature but are used less frequently. These address the disadvantages of batch experiments and thus offer a much more realistic approach. However, while batch experiments are sometimes considered to be quite material- and time-intensive, this disadvantage is even greater in conventional column experiments. To eliminate this disadvantage, the idea arose to simply miniaturise the experimental setup and conduct it using high-performance liquid chromatography (HPLC) equipment. Unfortunately, this idea has never been presented as an alternative to a high-throughput method, including data evaluation, and has certainly never been applied in the field of repository research. There have only been preliminary attempts so far. Therefore, in the next published study a method for conducting mini-column experiments (MCE) was developed and validated. During this, the retention of Cs(I) in two ionic strengths at C-S-H phases was investigated using the newly developed HPLC-MCE method and the results were compared with those from batch experiments. Furthermore, the method was further optimised to enable HPLC-ICP-QQQ (triple quadrupole inductively coupled plasma mass spectrometry) coupling, thus allowing online quantification of Eu(III) retention on kaolinite and sand, and with that making the method even more efficient [12] (and references therein).

As described, the retention of Mo(VI), Eu(III) and U(VI) in C-S-H phases has been extensively researched. In the context of a repository, however, the remobilisation of already bound analytes must also be considered. In the case of U(VI), this has been insufficiently researched, and for Mo(VI) and Eu(III) it has not been researched at all. Furthermore, the only data available comes from batch experiments and therefore, as already mentioned, does not realistically reflect the conditions to be expected. To be able to map dynamic conditions, a comprehensive MCE-study was conducted to quantify the dynamic

remobilisation behaviour of Si(IV), Ca(II), Mo(VI), Eu(III) and U(VI) from C-S-H phases. In this published study, those repository-relevant analytes were incorporated into the C-S-H phase/structure during synthesis and then remobilised under conditions also relevant to final disposal (high ionic strength, competing/displacing ions or cement additives); all using MCE [8] (and references therein).

In all studies described so far, and in most studies in literature, the sorption behaviour is evaluated by determining the analyte content in the supernatant solution (or eluate). If the analyte content in the solid itself were to be determined, additional validation of the sorption experiments would be possible. Such an approach is a method using laser ablation coupled to an inductively coupled plasma mass spectrometer (LA-ICP-MS), which offers a very good compromise: excellent detection limits with a large linear measurement range paired with spatially resolved analysis. It therefore makes sense to establish/adapt such an LA-ICP-MS method for quantifying traces of radionuclides in repository-relevant construction and backfill materials. However, due to several factors, such as matrix effects, the development of such an analytical method is not trivial [75-78]. The aim of a further (unpublished) study was to develop an LA-ICP-MS method for quantifying Si(IV), Ca(II), Mo(VI), Eu(III), and U(VI) (as model analytes) in C-S-H phases. During this, two known calibration concepts were adapted and, where necessary, further developed.

Overall, this work aims to gain new insights towards radionuclide retention and with that contributes to the safety assessment of a repository. During this, the retention mechanisms of repository-relevant elements on also relevant construction and backfill materials should be better understood. Furthermore, the method catalogue used to evaluate the retention and sorption capacities of this construction and backfill materials is to be expanded so that future questions can be answered more efficiently and in greater detail.

2. Current State of the Literature

2.1 High Level Nuclear Waste (HLW)

Although Henry Becquerel's discovery of radioactivity in 1896 is considered the beginning of modern radiochemistry, the anthropogenic enrichment of naturally occurring radioactive material (NORM) can be traced back much earlier, albeit involuntarily. When early humans began seeking shelter in caves, they unknowingly began accumulating NORM in increased amounts in their bodies, for example in the form of Rn. The development of human craftsmanship, the mining of minerals and ores, and the smelting of these into tools and weapons can, in a sense, be considered the beginning of industrial exposure to radioactivity. Thus, the discovery by Becquerel can be regarded as the beginning of the “conscious use” of radioactive processes and phenomena [79, 80].

To describe the further history of the anthropogenic use of radioactivity, Myasoedov and Kalmykov [81] have created an interesting chronological division. They divide the historical development and use of radioactivity into three periods. The first begins, as already mentioned, with Becquerel's discovery. According to Choppin et al. [80], however, it can also be traced back to Wilhelm Conrad Röntgen, who discovered X-rays in 1895. Based on this, Becquerel began his experiments to investigate the fluorescence of uranyl salts, which in turn led to the discovery of radioactivity. From here on, things moved quickly. Motivated by Becquerel's discovery, Marie and Pierre Curie provided proof of the ionising radiation of all U and Th compounds, which quickly led to the isolation of Po and Ra from pitchblende in 1898 (the latter in collaboration with Gustave Bémont). During this time and in the years after, until 1905, experiments by William Crookes, Becquerel, Ernest Rutherford, Frederick Soddy, and Friedrich Dorn proved that radioactive decay causes transformations in atomic nuclei, with the radioactive decay series being “genetically” linked. This was accompanied by the identification of β -radiation by Becquerel in 1900 and the identification of α -radiation by Rutherford in 1903 [80].

In the following years of the first period, there were numerous further discoveries, which cannot all be listed here. However, Rutherford's scattering experiments in 1911, which fundamentally changed our understanding of the structure of the atom, are particularly noteworthy. Also worth mentioning are the works of Kasimir Fajans, Soddy, and Joseph John Thomson around 1914, which provided evidence of isotopes. Thomson, for example, succeeded in quantifying two Ne isotopes, from which he concluded a natural distribution of 90% ^{20}Ne and 10% ^{22}Ne [80].

According to Myasoedov and Kalmykov [81], the transition from the first (1896–1949) to the second period (1940–1970) of radiochemical studies is rather fluent. While the first period describes the emergence and development of radiochemistry as an independent scientific discipline and thus deals with the discovery and exploration of fundamental laws of radioactivity, the core idea of the second period encompassed the practical mastery of nuclear energy, studies on the chemical properties of artificial elements, and the beginning of studies to solve the resulting problems, such as the disposal of radioactive waste [81]. Although Myasoedov and Kalmykov [81] date the beginning of the second period to 1940, it can be argued that the true beginning is more likely to be found in 1938, with the experiments of Otto Hahn and Fritz Strassmann regarding the induced fission of U after neutron bombardment [80]. Against the backdrop of historical injustice, the contribution of Lise Meitner and

Otto Frisch should be highlighted here. Hahn and Strassmann conducted the experiment but were unable to draw any clear conclusions from the data they collected. It was Meitner and Frisch who 1939 succeeded in a correct interpretation of the data, and with that ushering in the age of controlled fission of radioactive isotopes [80, 82, 83]. This inevitably led to a series of further experiments on nuclear fission, which culminated in the construction of the first reactor under the direction of Enrico Fermi 1942, as well as in the research conducted under the direction of Robert Oppenheimer in Los Alamos and the resulting detonation of the first atomic bomb in 1945 [80].

According to Myasoedov and Kalmykov [81], the third period of radiochemistry development began in the 1970s. In their seemingly rather dystopian worldview, ecological problems related to the protection of the environment from radioactive contamination and the storage of radioactive waste took on the highest importance. This view is strongly supported by the catastrophic events in Chernobyl (1986) and Fukushima (2011) [80, 81]. Apart from this, however, the positive achievements of this period should also be highlighted. Around 1970, at the beginning of the third period, Murray Gell-Mann's quark theory was developed and finally proven by Jerome Isaac Friedman, Richard Edward Taylor, and Henry Way Kendall. Another milestone in this journey of elementary particle physics was reached in 2013, when scientists at CERN succeeded in proving the existence of the Higgs boson [80].

It is clear, then, that the brief but content-rich journey through radiochemistry has brought humanity tremendous progress, but, as Myasoedov and Kalmykov [81] correctly pointed out, it has also brought a multitude of problems and challenges. One of the biggest of these is the final storage of radioactive waste. Since radioactivity is used in a wide range of areas today, different types of radioactive waste are produced. A classification system for these was established by the International Atomic Energy Agency (IAEA) [84]. This system, with its radioactive waste classes and their respective disposal types, is shown in Figure 1 and described in the following:

Exempt waste (EW) contains such low concentrations of radionuclides that no radiation protection measures are necessary. From the perspective of regulatory control, EW does not require further consideration, is therefore exempt and thus considered non-radioactive waste [84].

Very short-lived waste (VSLW) contains only radionuclides with very short half-life but with activity levels above the clearance limits. Therefore, VSLW is stored for a limited period (up to several years) for decomposition and as the activity falls below the clearance levels, it can be released from regulatory control in accordance with the conditions imposed. After that, it is considered as EW. The VSLW class includes waste that mainly contains radionuclides with very short half-lives, predominantly from research and medical purposes (e.g. from sources using ^{192}Ir and $^{99\text{m}}\text{Tc}$). Since the purpose of storage is to store the material until it has decayed to such an extent that it can be classified as EW and thus disposed of, one of the main criteria for classification as VSLW is the half-lives of the predominant radionuclides. However, there are no strict limits for this, although radionuclides with half-lives in the order of 100 days or less generally fall under this regulation [84].

Very low-level radioactive waste (VLLW) does not necessarily meet the criteria for EW but does also not require high levels of containment and isolation. VLLW has activity concentrations that only slightly exceed (if at all) the values for release from regulatory control and must therefore be considered from a radiation protection perspective. Therefore, specific landfill disposal sites with limited regulatory controls are entirely sufficient for the disposal of VLLW. These are very similar to conventional landfills for industrial waste but may include additional measures to cover the radioactive waste. Typical examples of VLLW include waste from the operation and decommissioning of nuclear facilities, such as soil and construction waste, but also waste from the mining or processing of ores and minerals, which may therefore contain naturally occurring radionuclides [9, 84].

Low-level radioactive waste (LLW) exceeds the clearance limits and usually contains short-lived radionuclides with higher activity concentrations or long-lived radionuclides, but only with relatively low activity concentrations. This means that during the period of confinement and isolation in/at the repository site, these radionuclides undergo significant radioactive decay. The classification of waste as LLW is therefore based on the respective radionuclides in the waste, with weighting given to possible exposure pathways for humans and nature. However, even at this level, LLW marks the lower limit for radioactive waste, which requires robust isolation and containment for periods of up to several hundred years. Near surface disposal sites are designated for this purpose, consisting of artificially created trenches or chambers located on the earth's surface or up to several dozen meters below ground level. One example of a source of LLW is the nuclear fuel cycle, which produces waste from the mining and processing of uranium and other materials containing significant amounts of NORM [9, 84].

Intermediate-level radioactive waste (ILW), due to its content of particularly long-lived radionuclides, requires a higher degree of containment and isolation than LLW. The boundary between LLW and ILW cannot be defined universally in terms of activity concentrations. Instead, the regulatory authority can therefore determine which waste is to be classified on general safety evidence until ILW repositories are established. One distinguishing feature is that ILW can contain larger quantities of long-lived radionuclides, in particular alpha-emitting radionuclides, which do not decay to a level of activity acceptable for near-surface disposal even over a longer period of time (> 300 years). However, the ILW repository requires no or only limited heat dissipation measures, although the type and extent of the general measures depend on the properties of the ILW. Potential repositories range from caverns or vaults several tens' meters deep to tunnel-based repositories several hundred meters deep (similar to mining facilities). Like VLLW and LLW, ILW is also produced during reactor operation, decontamination, decommissioning, and other activities in the nuclear fuel cycle. In the case of ILW, this includes, for example, contaminated filter materials or residues from recycling or recovery processes [9, 84].

High-level radioactive waste (HLW) is defined as waste that contains both short-lived and long-lived radionuclides in such high concentrations, compared to ILW, that it poses such a high risk to humans and the environment that a higher level of containment and isolation is required. Since HLW generates considerable amounts of heat through radioactive decay and releases this over several centuries, heat dissipation is also an important factor that must be considered when planning a HLW repository. Due to the high requirements for containment and isolation, HLW is intended to be disposed in intact and stable deep geological formations several hundred metres below the surface. One option here would

be a borehole-like disposal in deep geological repositories (see Chapter 2.2). The main origin of HLW is at the end of the nuclear fuel cycle, with spent fuel elements from nuclear power reactors. Until final disposal facilities for HLW are established, national authorities may, for communication purposes, determine on the basis of generic safety assessments that certain waste is to be classified as ILW or HLW [9, 44, 84].

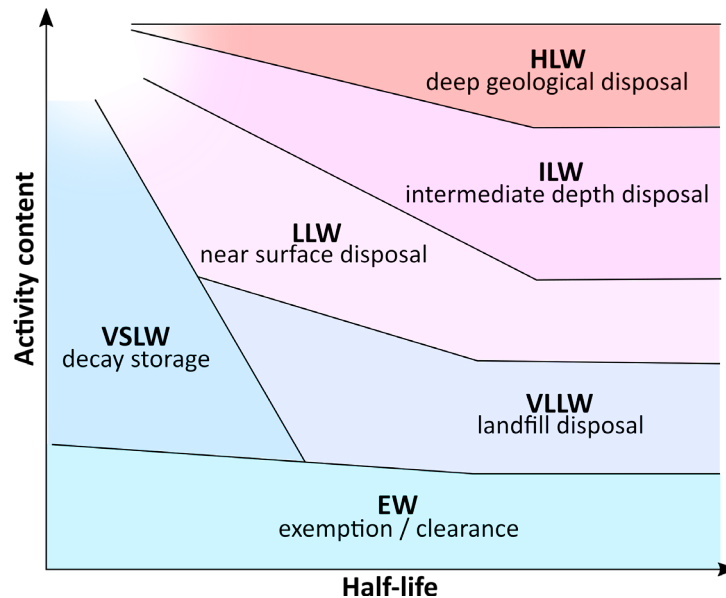


Figure 1: Presentation of the waste classification system and the respective designated repository/disposal types; adapted from IAEA GSG-1 [84].

As has been shown, the discovery of radioactivity has led to the development of numerous new technologies involving radioactive processes, such as the operation of nuclear power plants for electricity generation. This branch of utilisation alone produces a large amount of radioactive waste, which must be disposed or stored in final repositories. Several examples of this have already been mentioned. However, all these final storage options have one principle in common: *“The preferred strategy for the disposal of all radioactive waste is to confine it (i.e., to confine the radionuclides within the waste matrix, the packaging, and the disposal facility) and isolate it from the accessible biosphere [9].”* To achieve this, a safety assessment is essential in all respects and, due to the high hazard potential, especially for high-level waste [9, 85].

2.2 Repository in Germany

In Germany, the safety assessment, the planning, and construction of a HLW repository are subject to several laws. One of these is the “*Act on the Search for and Selection of a Site for a Repository for High-Level Waste*” (Standortauswahlgesetz - StandAG); in the version of 22.03.2023 [10]. This law regulates the repository site selection process and is thus intended to ensure “*a site with the best possible safety for a final storage facility in accordance with Section 9a (3) sentence 1 of the Atomic Energy Act in the Federal Republic of Germany for high-level radioactive waste generated domestically in a participatory, science-based, transparent, self-questioning, and learning process* [10].” The exact wording of the StandAG is as follows (translated from German):

“The radioactive and other pollutants in the waste must be concentrated and enclosed in a containment-effective rock area or, in accordance with § 23 (1) in conjunction with (4), in final storage concepts based primarily on technical and geotechnical barriers within these barriers, with the aim of keeping these substances away from the biosphere. For a period of one million years, with regard to the protection of humans and, insofar as the long-term protection of human health is concerned, the environment, it must be ensured that exposure due to releases of radioactive substances from the final repository is negligible compared to natural radiation exposure [10].” Furthermore, the StandAG stipulates “*that it must be possible to recover the stored waste during the operational phase and that sufficient precautions must be made for the possible recovery of the waste for a period of 500 years after the planned closure of the repository* [10].”

To fulfil this aim, the StandAG defines that in Germany, rock salt, clay rock, and crystalline rock are generally suitable as host rocks for a HLW repository. In this context, it was also stipulated that “*the surface of a containment effective rock zone must be at least 300 meters below the ground surface*” and “*must be at least 100 meters thick.*” In the current version of the StandAG, a final decision on the location is expected by 2031 [10].

In addition to the regulatory legislation, many research and development (R&D) projects dealing with the issue of a German repository have been and continue to be funded. One of these was the joint project “ANSICHT” (2012 to 2017) – involving the Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) gGmbH, Federal Institute for Geosciences and Natural Resources (BGR) and DBE TECHNOLOGY GmbH. As part of the ANSICHT project, two generic geological site models were used to develop an initial draft methodology for the safety assessment of a HLW repository in northern and southern German clay formations (taking all legal requirements into account). The two location site models, “NORD” and “SÜD”, are the basis for calculations that are intended to demonstrate the integrity of the containment providing rock zone (CRZ) and prove radiological safety. To do so, it was necessary that a numerical proof is a part of the safety verification/assessment concept. This numerical verification of CRZ integrity, on the other hand, requires comprehensive knowledge of the thermal, mechanical, hydraulic, chemical and biological properties of the host rock formation. The result was a three-dimensional geological model that depicts the key formations and (hydro-)geological conditions of the area under investigation [3, 4, 7, 86].

Another key component of ANSICHT was the creation of FEP (Features, Events, and Processes) catalogues and scenario development to evaluate possible future evolutions of the final repository system. During this, criteria for the integrity verification of the geological and geotechnical barriers and the radiological safety statement were explained. A specific FEP catalogue for each model describes the initial state and the future processes of the repository system and was structured in such a way that it enables systematic scenario development and the representation of direct dependencies between the FEPs. It includes an FEP screening to identify irrelevant FEPs based on their conditional probability of occurrence and their impact in four subsystems (near-field, host rock, drifts and shafts, host rock). The “NORD” FEP catalogue, for example, is not directly transferable to other location site models, but represents a characteristic situation in the Lower Saxony Basin and served as the basis for an exemplary scenario development [3, 4, 7].

Based on the site models developed in ANSICHT (“NORD” and “SÜD”), a specific safety case for a repository in Germany can now be developed, individual components can be analysed and evaluated for a period relevant for a repository. An important aspect here, is the geochemical interaction of the radionuclides with the construction and backfill materials in the near field of the repository [3, 4, 87]. Analogues to the model-specific FEP catalogue (see above), it is difficult to provide a generally valid proof of safety for different site models. For this reason, the analysis in this work is orientated/limited on/to the location site model “NORD”.

The “NORD” model represents a typical situation in the North German Basin [3, 4, 7, 11]. Figure 2 shows (in purple) the pre-tertiary claystone formations that are generally suitable for a potential repository in northern Germany [88]. According to NORD, the reference region and its surroundings are typically divided into a crystalline basement, a top layer of sedimentary rock and Quaternary sediments. The thick clay formations of the Lower Cretaceous (Hauterivian and Barremian) with a thickness of approx. 550 m were selected as potential host rock. These consist of claystone and clayey marl as well as subordinate micritic limestone marl and lie at a depth of 300 to 1000 m below ground level. The Hauterivian is widespread, with a total thickness of 200 to 300 m, consists of alternating layers of limestone, limestone marl beds with illite, kaolinite-bearing claystone and clay marlstone beds. The Barremian, is also widespread, with a total thickness of 200 to 400 m, and consists of partly weakly bituminous claystone to clay marlstone. The upper geological layers contain fresh water, while the deeper aquifers in the Rhätsandstein, Aalensandstein and Hilssandstein formations show higher salinity [3, 4, 7, 11].

To avoid any adverse impact from the surface, the repository mine is designed for an emplacement level at a depth of approx. 750 m below ground level and requires an area of approx. 7.6 km². The general layout of the repository is based on earlier designs by Pöhler et al. [89] and considered an emplacement floor, infrastructure area for excavation work, waste transport and ventilation. However, the volume of excavations would be minimised to reduce potential disturbance and maintain the integrity of the host rock [3, 4, 7, 89, 90].

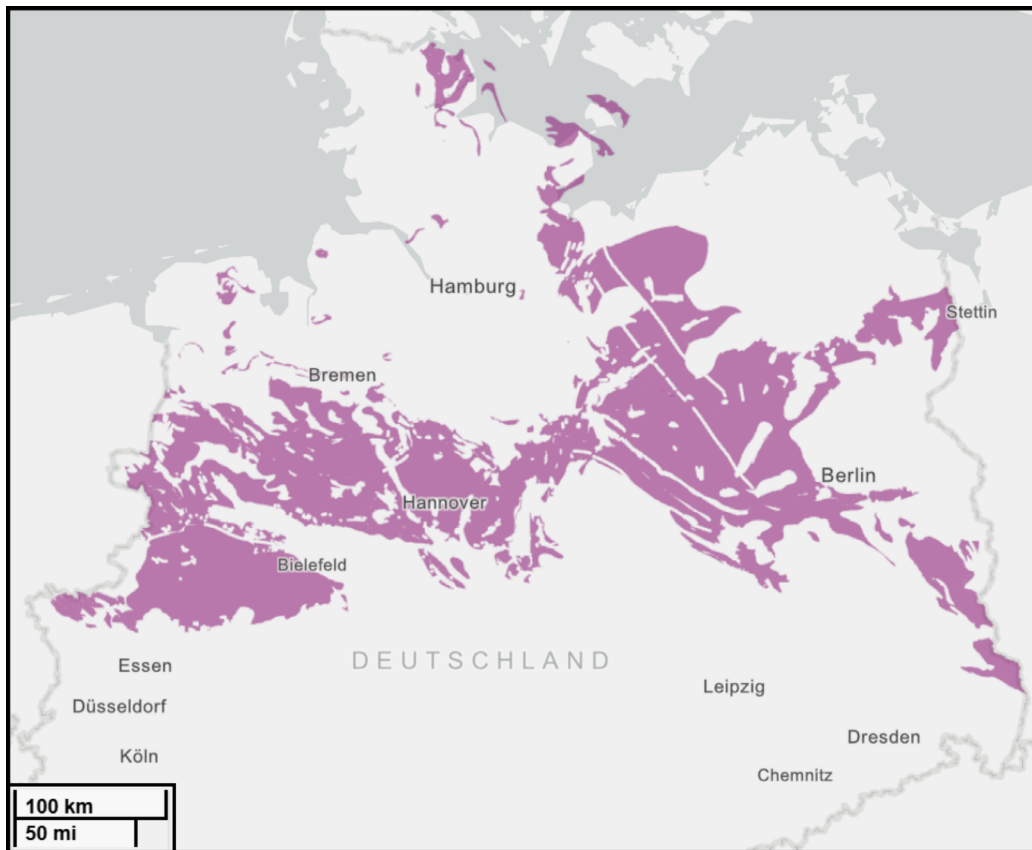


Figure 2: Map showing the pre-tertiary claystone formations in northern Germany that are generally suitable for a final disposal site (in purple); graphic/screenshot (with permission) of the interactive map on the BGE (Bundesgesellschaft für Endlagerung mbH) website, Copyright (2026) Bundesgesellschaft für Endlagerung [88].

In the “NORD” model, due to the sufficient thickness of the Lower Cretaceous clay formations, the possibility of vertical borehole storage/emplacement was analysed and found to be feasible. The access tunnels to the storage/emplacement boreholes are to be 400 m long and contain either 20 boreholes for non-heat-generating waste or 13 boreholes for heat-generating waste. [4]. Figure 3 shows schematically a filled and sealed disposal borehole and thus the multi-barrier system. The latter consists of a variety of sub-components: the waste mould, the containers, the backfill- and buffer materials and a borehole plug. Together, these components are intended to delay and ideally prevent the release of nuclides from the HLW into the host rock of the repository [3, 4, 7, 11].

The 27 m deep boreholes are equipped with an inner and outer liner for stability and retrievability. Three canisters are inserted into the inner liner; the remaining cavity is filled with sand. The space between the inner and outer liner is filled with a compacted clay buffer material, which consists of a bentonite-sand-mixture. This Buffer material is intended to protect the canisters from contact with water and should provide a good diffusion barrier for radionuclides escaping from the HLW canisters. The outer liner stabilises the excavation and the buffer, and absorbs the pressure caused by rock movements. The sealing concept for “NORD” comprises shaft seals, drift seals (in the infrastructure area and in the emplacement fields) and borehole seals. The borehole seals consist of a bentonite sealing element and a concrete abutment. Route seals (migration barriers) to the emplacement fields

in “NORD” contain a bentonite sealing element, which is clamped by two concrete abutments. Shaft closures are adapted to the geological conditions and include watertight linings that can extend into the barren ground, as well as sealing systems made of bentonite and bitumen-filled gravel columns at various depths to separate aquifers [3, 4, 7, 90].

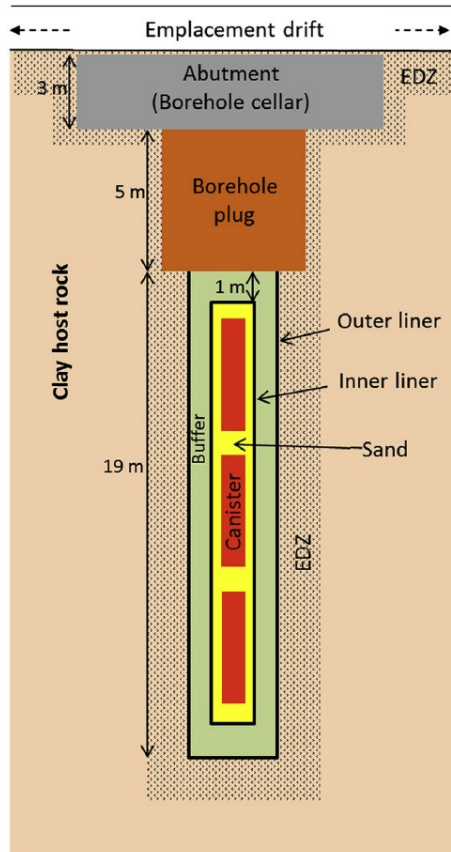


Figure 3: Schematic presentation of the structural design of an emplacement borehole according to the location site model “NORD”; EDZ = excavation damaged zones; by Jobmann et al. [4] (based on Lommerzheim and Jobmann [90]); reprinted from *Journal of Rock Mechanics and Geotechnical Engineering*, 9, Safety assessment methodology for a German high-level waste repository in clay formations, M. Jobmann et al., 856–876, Copyright (2017), published under CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>) [4].

As described, the scenario development in the ANSICHT project was originally carried out using the FEP catalogue of the location site model “NORD”. However, it was found that this catalogue was still at a development stage at that time, containing overlapping features and aggregated processes. This led to ambiguities and over-descriptions, which later motivated a methodological revision to compile the FEP catalogues [3, 4, 7]. To evaluate and further develop the methodology gained from ANSICHT, the Project Management Agency Karlsruhe (PTKA) commissioned by the (formerly) Federal Ministry for Economic Affairs and Energy (BMWi) commissioned BGE TECHNO-LOGY GmbH, BGR, and GRS with the joint project ANSICHT II (2018 to 2022). Individual points from ANSICHT were revised and reevaluated within the framework of adapted and new regulations. One of the key findings is that, for the type of repository considered in the location site model NORD (in a thick claystone formation), the safe confinement of radionuclides can generally be expected to be guaranteed [11, 86].

2.3 Cement and its Alteration

As outlined above, the final disposal of HLW is planned in deep geological formations in order to effectively protect future generations from the harmful effects of radionuclides and their fission products. In a potential HLW repository (especially in the “NORD” model), cement-based materials such as concrete are primarily used as shotcrete to secure the tunnel contour and as abutment material in conjunction with sealing structures. A rough distinction can be made between the following uses [2-4, 7, 10, 11, 13, 90]:

Stabilisation of facilities: All mine facilities that are open for long times, such as shafts, infrastructure areas (e.g. emplacement drifts), and connecting tunnels, should be stabilised and sealed with concrete lining.

Borehole closures: A borehole closure, especially in the “NORD” model, consists of a bentonite sealing element and a concrete abutment, which serves a stabilisation of the bentonite sealing element.

Tunnel closures: These migration barriers are placed in the crosscuts before the junctions with the main tunnels and, in the “NORD” repository concept, consist of a bentonite sealing element clamped between two concrete abutments.

Shaft closures: Like the migration barriers, concrete abutments are also used to stabilise bentonite sealing elements in the shaft closures.

Concrete or cement (Latin: “opus caementitium”) was already used in ancient times, for example in the Roman Pantheon or harbours [91]. As a brief excursion, a few semantic terms need to be clarified here: Cementitious materials include, for example, hydrated cement grout, concrete, and mortar. All of these materials can be used in a HLW repository in the scenarios described above. In this case, the cement itself is the hydraulic binder that holds other materials together [13]. It should also be noted that there are two important groups of cement binders: hydraulic and polymer cements. Hydraulic cement is mixed with water and reacts with it to form a new water-containing compound (hydrate), which conglomerates the surrounding surfaces of other materials. In polymer cements, on the other hand, increasing cross-linking (initiated by catalysers or irradiation) of the molecules involved leads to solidification. However, hydraulic binders are preferred for the production of ceramic materials, the most important of which is Portland cement [91]. In this context, a mixture of cement hydrate, water, and fine additives is called mortar, while concrete is a mixture of water, cement hydrate, and coarse and fine additives. Cement is therefore at the heart of many construction and filling materials, and also dominates their chemistry [13].

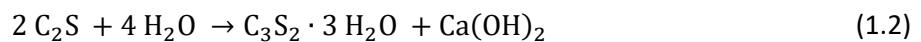
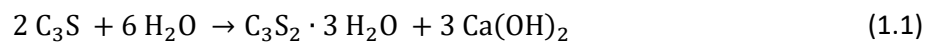
In addition to its use as a construction and backfill material, cement can also be used as a stabilisation/solidification (S/S) technology. Those cement-based S/S systems can be used for the chemical fixation and encapsulation of a wide range of waste forms, which include organic or inorganic industrial wastes, soils contaminated with toxic metals and organic components, incineration residues, and bulk wastes from the power generation industry – for example electroplating sludges or even radionuclide waste. In this case, ordinary Portland cement (OPC) is usually used alone or in combination with cement substitutes as a binder [92] (and references therein). It is therefore clear from the outset that cement-based construction and backfill materials are not only useful as such in a HLW repository

but can also actively serve as a sorption barrier for radionuclides. This fact has already been proven in a large number of studies and publications, the vast majority of which have always assumed OPC and its alteration products [11, 13, 14, 19, 34, 72, 74].

To produce the most common type of cement (OPC), limestone (CaCO_3) is usually heated to around 1450°C in a kiln together with clay. To put it simply, it can be said that only minerals rich in CaO and SiO_2 are mixed and fired during cement production; this allows the basic components CaO , Al_2O_3 , SiO_2 and Fe_2O_3 to be derived [13, 91]. Depending on the composition and temperature during firing, different clinker phases are obtained. The resulting phase diagram is very complex and will not be discussed in detail here but for those who are interested, it can be found in Hornbogen et al. [91] starting on page 340. It is important to note that at temperatures between 1400 and 1500°C , the reaction of CaCO_3 with silicon-containing minerals produces a mixture of several anhydrous minerals, mainly calcium silicates. The hard cement clinker produced during the burning process is then ground into a powder with a small amount of gypsum. The four most important phases of cement/OPC are [13, 91]:

- 50–70% alite, a tricalcium silicate, C_3S ($\text{C} = \text{CaO}$ and $\text{S} = \text{SiO}_2$), which reacts with water to form calcium silicate hydrate (C-S-H) and portlandite ($\text{Ca}(\text{OH})_2$). During this hydration, the C_3S leads to rapid, continuous hardening at a low heat of hydration and is therefore a desirable phase in Portland cement. Based on the phase diagram mentioned above, this phase is only stable between 1250 and 2070°C . Hence the choice of firing temperature [13, 91, 93, 94].
- 20–30% belite, a dicalcium silicate (C_2S), which also reacts with water to form C-S-H and $\text{Ca}(\text{OH})_2$, but at a slower rate [13, 91, 93, 94].
- 5–12% aluminate, tricalcium aluminate C_3A ($\text{A} = \text{Al}_2\text{O}_3$), which reacts with water in the presence of a sufficient amount of gypsum to form AFt phases (calcium aluminosulphate), such as ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) [13, 91, 93-95].
- 5–12% ferrite, a calcium aluminoferrite, $\text{C}_2(\text{F},\text{A})_5$ ($\text{F} = \text{Fe}_2\text{O}_3$) with a high proportion of Fe instead of Al, which reacts with water in a similar way to C_3A [13, 91, 93, 94].
- Approximately 2% gypsum, which most commonly occurs as dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4), is added to slow down the setting time and increase the duration of workability [13, 91, 93, 94, 96].

To prepare concrete for a potential HLW repository, cement must be mixed with water and other aggregates. When water is added, the previously anhydrous cement clinker undergoes a series of hydration reactions and develops binding properties and strength [13]. Examples of such hydration reactions are shown in Equations 1.1 to 1.3 – according to Hornbogen et al. [91].



The hydration reactions lead to the formation of Ca(OH)_2 , C-S-H phases, and other secondary phases containing aluminium, iron, and sulphate, among other things (see above). If the cement particles are small enough and the amount of water added is sufficient, this reaction proceeds completely. Taking into account the above-mentioned proportions of the Portland cement clinker phases, the resulting hydrate phases and the claims made by Berner [97], it can be said that the hydrated cement must consist to 60–75% of a C-S-H- Ca(OH)_2 mixture [13, 91, 97]. Since, most HLW repository studies assume the use of Portland cement-based concrete, crystalline portlandite and C-S-H phases are mainly assumed to be the cement solid phases [11, 13, 14, 34, 72, 74, 98].

Solutions in equilibrium with hydrated cement are hyperalkaline ($\text{pH} \geq 13$) and, in contact with penetrating pore water, hydrated cement is not thermodynamically stable and tends to corrode. With other words, hydrated cement minerals, and particular the C-S-H phases, are not in thermodynamic equilibrium with penetrating pore water and therefore partially dissolve or decompose over time. This results in cement ageing phases, which consist essentially of C-S-H phases. Figure 4 schematically shows the ageing pattern of hydrated cement. Here, a progressively lower pH value of the pore water describes four discrete states of the cement degradation (state I–IV) [13, 16-19, 99-101].

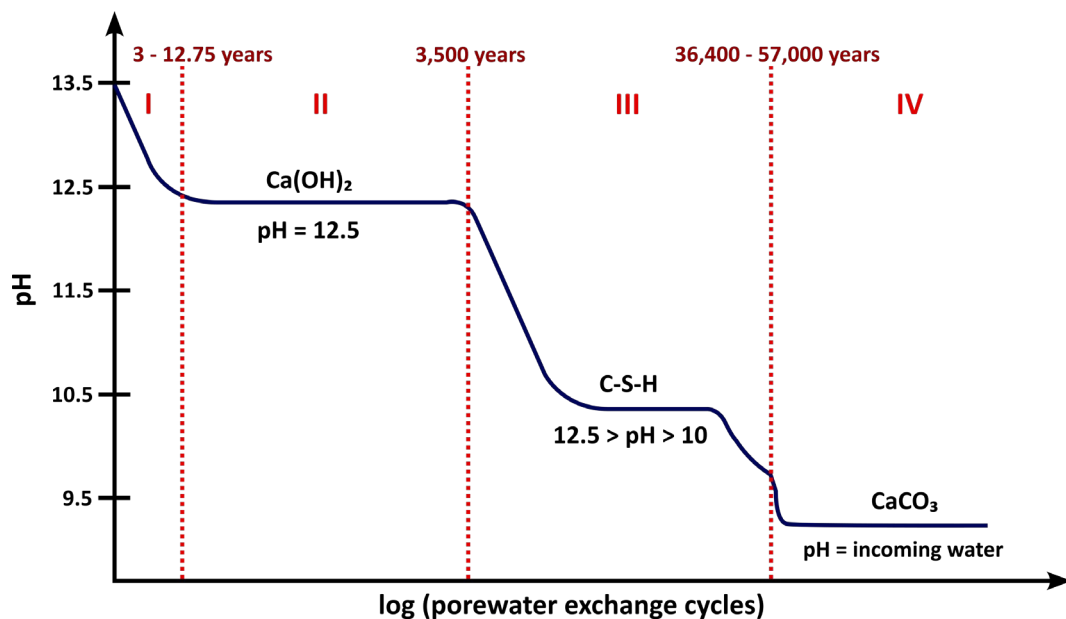


Figure 4: Schematic representation of the 4 states of cement alteration, in terms of the pH value development of the cement pore water (25°C) in contact with hydrated cement; the scales of the pH value and the pore water exchange cycles are indicative and depend on many factors, such as the pore water replacement rate or the temperature; adapted from *Cementitious Materials and Their Sorption Properties*, M. Ochs, D. Mallants, and L. Wang, Springer Nature, 2016, reproduced with permission from Springer Nature [13]; with additional data on time scales from Jacques et al. [25].

In state I, the composition of the pore water, which is in contact with hydrated cement, is dominated by Na^+ , K^+ and OH^- ions. The high concentration of these ions results from the dissolution of alkali metal sulphates and the necessary charge equalisation of the system, which results in the corresponding concentration of hydroxide ions. The pH value is thus controlled by the dissolution of alkalis and is consequently very high, with pH values of 12.5 to 13.5. The free sulphate ions are intercepted/absorbed

by the AFt and AFm phases present. As the solubility of Portlandite is low at such pH values, only small amounts of Ca^{2+} ions are leached [13, 25, 97]. According to the modelling carried out by Jacques et al. [25], a duration of 3 to 12.75 years can be expected for this state

After all alkali ions have been leached out, state II begins, in which the pH value of the pore water is determined only by the solubility of portlandite. The chemistry of the pore water in this state is only controlled by the dissolution of the cement phases but essentially consists of a 20 mM $\text{Ca}(\text{OH})_2$ solution with a pH of 12.5. The duration of this state is proportional to the amount of portlandite available [13, 25, 97] and, according to Jacques et al. [25], ends after approx. 3,500 years.

After complete dissolution of the portlandite, the most complex of the 4 states follows, state III. The element composition and the pH value of state III are controlled by a chain of dissolution and precipitation reactions of the C-S-H, AFm and AFt phases. The chemistry of the pore water is primarily determined by the incongruent dissolution of the C-S-H phases. At the beginning of state III, the C-S-H phases have a molar calcium to silicon ratio (C/S) of > 1.5 , whereby the C/S ratio and the pH value increasingly decrease as this state progresses. The C/S ratio decreases from 1.5 to 0.8 and the pH from 12.5 to 10 due to the leaching of $\text{Ca}(\text{II})$. The semi-crystalline structural properties of the C-S-H phases and the dissolution and precipitation processes involved make the transformation of the C-S-H phases a very complex process, which makes it difficult to provide precise information [13, 22-24]. One example for this is provided by Atkins and Glasser [14], who report that the pH value of the pore water in state III with a C/S of 0.8–1.5 should be in a range of 11.0–12.4. Towards the end of state III, a congruent dissolution of the semi-crystalline, disordered tobermorite-structured end member of the C-S-H phases ($\text{C/S} \approx 0.8$) is generally assumed, whereby a fixed pH value of 10 is established [13, 23-25, 102, 103]. According to Jacques et al. [25] this state ends after 36,400 to 57,000 years.

State IV marks the end of cement ageing process. At this point, hydrated cement phases are completely dissolved, and the pH drops to a value below 10. The composition of the pore water is now only determined by the remaining rock minerals and the inflowing water - in the case shown in Figure 4, this is calcite [13, 25, 97].

2.4 C-S-H Phases

Based on the literature described so far, it can be said that C-S-H phases make up the largest proportion of hydration phases and can be regarded more or less as the last bastion of cement ageing. C-S-H phases are therefore the most important component of both, aged and freshly hydrated cement. If potentially leaking radionuclides are to be retarded by one of the barriers present in the near field of the repository, C-S-H phases can play an important role and must therefore be considered a the safety assessment.

Due to their almost amorphous, semi-crystalline structure, C-S-H phases are often described as cement gel [13]. Structurally, however, the C-S-H structure is described quite well in the review article by Papatzini et al. [22]:

Here, too, the C-S-H phases are described as the main product of cement hydration and the primary binding phase. They are an almost amorphous or, in other words, highly disordered material, although the morphology of C-S-H phases has not yet been fully clarified. In the course of elucidating the structure of C-S-H, a large number of models were proposed; the most common ones are the layered and colloidal structures [22] (and references therein).

In the layered (crystal-like) model, C-S-H phases are assumed to be similar to naturally occurring layered silicates. One Example is the Feldman-Sereda model, where the C-S-H structure is described as intertwined layers with pores and interlayer water in between. Here, like in other layered models, a tobermorite structure is assumed for the layered domains, which consists of CaO layers reinforced with silicate chains [22] (and references therein). Figure 5 shows a schematic drawing of the Feldman and Sereda Model.

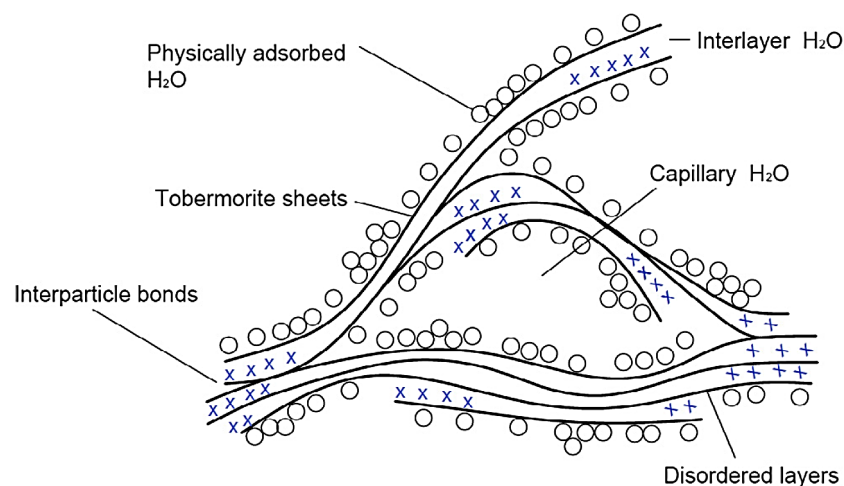


Figure 5: Schematic drawing of the Feldman and Sereda Model [104] by Papatzani et al. [22]; reprinted from *Constr. Build. Mater.*, 74, A comprehensive review of the models on the nanostructure of calcium silicate hydrates, S. Papatzani, K. Paine, J. Calabria-Holley, 219–234, Copyright (2015), with permission from Elsevier [22].

In the colloidal model, C-S-H phases were initially considered as a colloidal, nanocrystalline gel whose basic units are spheres with a diameter of about 5 nm. Depending on the model, these beads are assumed to assemble in two different packing densities, forming two types of C-S-H domains: High- and Low-Density C-S-H. In a later elaboration of colloidal models, it was suggested that the beads themselves have a layered internal structure. In most cases, a tobermorite and jennite phase/structure was assumed [22] (and references therein). An example for a later stage colloidal model was described by Jennings [105] using the Colloidal Model II (CM-II). A schematic representation is shown in Figure 6. This model is described as a granular model that is a combination of the Feldman-Sereda model and the colloidal model. It attempts to combine the strengths of both approaches [22, 105].

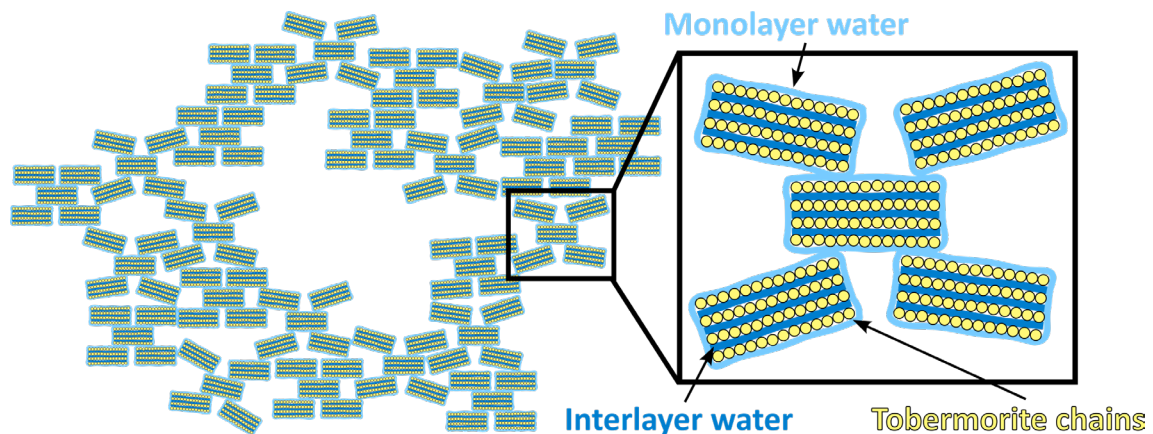


Figure 6: Schematic drawing of the CM-II Modell after Jennings [105] and Papatzini et al. [22].

In general, literature suggests that C-S-H phases are almost amorphous for X-ray diffraction (XRD) and can therefore be considered as "cement gel". Although the XRD data described in the literature suggest an amorphous character, a low crystallinity should also be recognisable. Despite all the results, data and considerations regarding the structural composition of the C-S-H phases, the amorphous to semi-crystalline nature and a detailed possible crystal structure is difficult to determine with certainty [13, 22]. But the crystalline structure of C-S-H phases and thus corresponding XRD data are reported in several publications. Depending on the preparation routine, different crystal structures are reported – as can be seen, for example, in Kee et al. [20]. The most common synthesis route for C-S-H phases – especially in the context of retention experiments in repository research - is the co-precipitation from an aqueous solution/suspension with CaO and SiO₂ as precursors [8, 17, 20, 30, 99, 106]. The C-S-H phases synthesised in this way are predominantly described as a semicrystalline cement gel with either a 11 Å or 14 Å tobermorite structure (also featured in Chapter 3.1.3) [8, 16, 20, 21].

In addition to synthesis on a laboratory scale, it is also possible to purchase C-S-H phases commercially. For example, the company Cirkel (in Emsdette, Germany) offers its product Circosil®, which is an excellent cost- and time-saving alternative to synthesised C-S-H phases. Cirkel states, that Circosil® consists of 88 % tobermorite phases ($5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$), 10 % embedded SiO_2 and traces (<0.5% each) of Al-, Mg-, Fe-, Ti-, K-, Na-, Zr-, Mn- and Cr-containing minerals. With this information and additional XRF (X-ray fluorescence spectroscopy) data provided by Cirkel, a C/S ratio of approximately 0.65 can be calculated. However, if only the tobermorite content is used as the basis for calculation, the C/S ratio is 0.83 [12, 107, 108]. In view of the above properties, Circosil® can be considered a suitable model substance for C-S-H phases at the end of the alteration process.

In the work published by Grangeon et al. [21] the tobermorite-like structure of C-S-H and its dependency in relation to the C/S ratio was described very well: When developing the C-S-H structure as a function of the C/S ratio, early models assumed that the crystal structure of tobermorite was similar to C-S-H phases with a C/S ratio below 1.3, whereas Jennite analogues were assumed at higher C/S ratios. Both minerals are layered structures of Ca-polyhedra (7-fold coordination in tobermorite and 6-fold in jennite) featuring wollastonite-type Si chains on their surface. These layers are usually separated by a hydrated interlayer, which in turn is associated with cation intercalations. In contrast, there is a model according to which a tobermorite-like structure is assumed, regardless of the C/S ratio [21, 102, 109, 110]. A sketch of the C-S-H structure based on the tobermorite model proposed by Grangeon et al. [21] is shown in Figure 7.

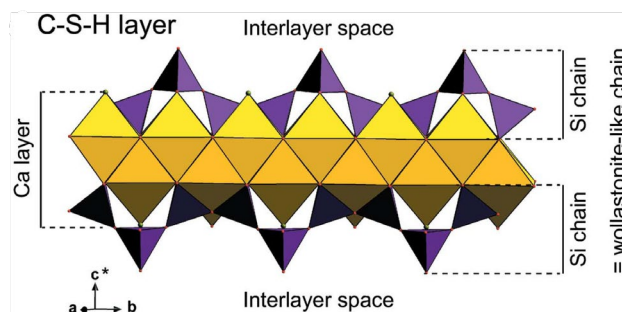


Figure 7: Sketch of the tobermorite-like C-S-H structure proposed by Grangeon et al. [21]; reprinted from J. Appl. Crystallogr., 49, Structure of nanocrystalline calcium silicate hydrates: insights from X-ray diffraction, synchrotron X-ray absorption and nuclear magnetic resonance, S. Grangeon et al., 771–783, Copyright (2016), licensed under CC BY 2.0 UK (<https://creativecommons.org/licenses/by/2.0/uk/>) [21].

Part of the tobermorite-like model involves varying amounts of $\text{Ca}(\text{OH})_2$. It is assumed that C-S-H and $\text{Ca}(\text{OH})_2$ form a kind of nanocomposite, with interlayering of C-S-H and $\text{Ca}(\text{OH})_2$ suspected at higher C/S ratios. Based on the work of Grangeon et al. [21], the C/S ratio has the following effect (shown in Figure 8): At low C/S ratios, the structure is described as a “nanocrystalline turbostratic tobermorite having corrugated layers” but as “the Ca/Si ratio increases, Si bridging tetrahedra are progressively removed”. When increasing the C/S ratio, the weakened layer to layer binding leads initially to an increased interlayer distance. However, as the C/S ratio continues to rise, more Ca is incorporated into the interlayers, which in turn acts as a (new) bridge between these and reduces the interlayer distance

again. If the C/S ratio is increased further ($C/S > 1.5$), the Ca coordination spheres ultimately combine and form a Ca(OH)_2 structure in the interlayer. However, this type of structure could not be observed in their study, as all samples contained some Si bridging tetrahedra and, in some studies, the structure of the C-S-H phases with the lowest C/S ratio did not allow the bonds between adjacent layers to be observed. At very high C/S ratios (> 1.5), however, the precipitation of Ca(OH)_2 outside the C-S-H structure has been reported [21] (and references therein).

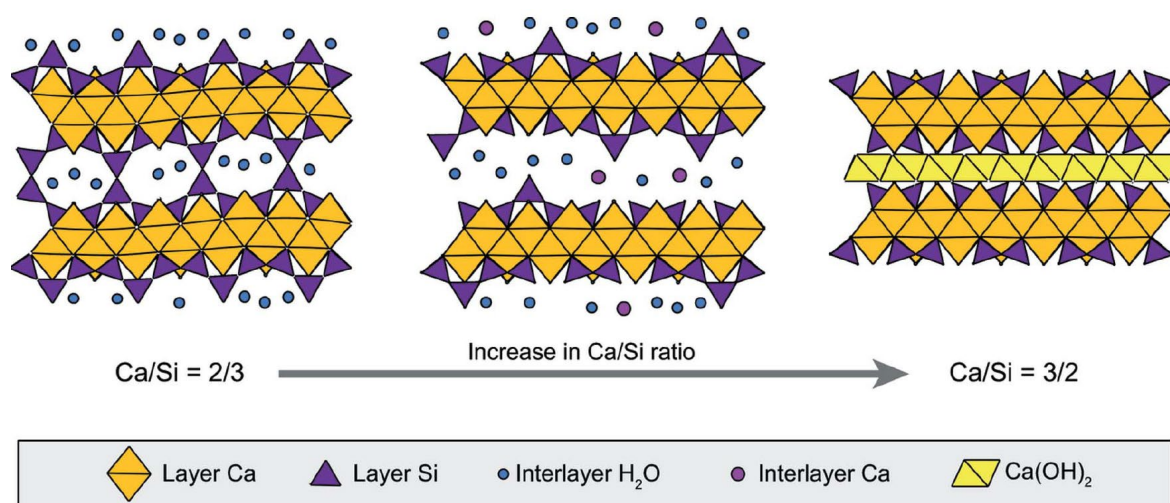


Figure 8: Evolution of C-S-H structure as a function of its C/S ratio proposed by Grangeon et al. [21]; reprinted from *J. Appl. Crystallogr.*, 49, Structure of nanocrystalline calcium silicate hydrates: insights from X-ray diffraction, synchrotron X-ray absorption and nuclear magnetic resonance, S. Grangeon et al., 771–783, Copyright (2016), licensed under CC BY 2.0 UK (<https://creativecommons.org/licenses/by/2.0/uk/>) [21].

In addition to the effects of the C/S ratio on the crystal structure, there is another important correlation regarding the zeta potential. As already mentioned, in C-S-H phases with a high C/S ratio, more Ca is incorporated into the structure, which in turn results in a positive surface charge and preferential adsorption of anions. As the C-S-H phases age, the C/S ratio decreases (see Chapter 2.3), the surface charge becomes neutral at a $C/S \approx 1.2$ and is negative at even lower C/S ratios. At this point the C-S-H phases are preferred primarily for the sorption of cations [13, 14].

Equally important is the fact that the pH value of the pore water surrounding the C-S-H phases is dictated by the C/S ratio. This causality was described very well by Baston et al. [24]. Figure 9 shows the relationship between the pH value and the C/S ratio. In this context, Baston et al. [24], also using data from Harris et al. [111], report that C-S-H phases with a C/S ratio of > 0.8 preferentially leach Ca (compared to Si). However, if a C/S ratio of ≈ 0.8 is reached in the remaining solid phase, the C-S-H phases leach congruently. The same applies to the reverse scenario, in which a C/S ratio of < 0.8 is present. In this case, the C-S-H phases preferentially leach Si (compared to Ca) until a C/S ratio of approx. 0.8 is reached again, followed by congruent leaching [24]. This relationship is also shown in Figure 9 by arrows.

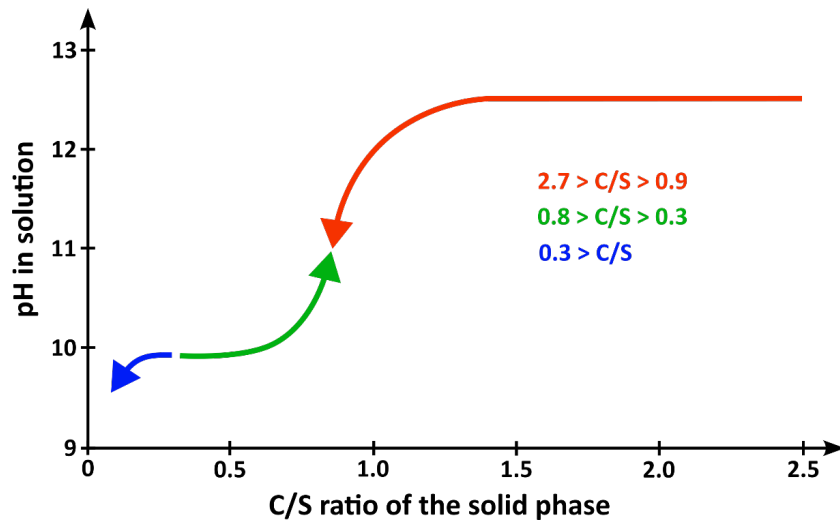


Figure 9: Graphical representation of the relationship between the pH value of the pore water depending on the C/S ratio of the respective C/S phase at 25°C; the arrows indicate the development of the C/S ratio during successive equilibration with water; adapted from Baston et al. [24] (and references therein).

In summary, it can be concluded that C-S-H phases are among the most important cement clinker and alteration phases. They can be understood as a semi-crystalline and simultaneously colloidal cement gel. Depending on the degree of alteration and, as a result, the C/S ratio, the pH value of the porewater and the adsorption properties of the C-S-H phases change dramatically, with anions being adsorbed preferentially at the beginning and cations being adsorbed preferentially later on. However, because of their semi-crystalline, colloidal and gel-like morphology, C-S-H phases offer a variety of adsorption sites for both anions and cations - depending on the degree of alteration. Thus, understanding the retention behaviour of repository relevant elements in cement-based materials – especially C-S-H phases – under geochemical conditions is of great interest for a repository safety assessment.

2.5 The Term Retention and Mathematical Models

When performing experiments investigating the retention/adsorption behaviour of analytes on, for example, solid powder-like materials, it is important to know all possible interaction mechanisms (of analytes with the adsorbent) to interpret the results accurately. As being discussed in the Chapter 2.6, the elements investigated show a broad range of possible retention mechanisms in the near field of a potential repository: adsorption, intercalation, substitution or (surface-/co-) precipitation. Therefore, a basic understanding of adsorption processes should be provided first.

In general, the accumulation of dissolved substances at interfaces is referred to as adsorption. The physical state of the interfaces is primarily irrelevant (e.g. liquid-liquid or liquid-solid). If the adsorbed substance is released from the interface again, i.e. returns to solution, this is referred to as desorption; in other words, the opposite process to adsorption [112, 113]. Due to the problem addressed in this work, the following will mostly assume liquid-solid interfaces, i.e. the adsorption of dissolved particles on solids.

To better understand the following explanations, the necessary nomenclature will be briefly discussed at this point, where three key terms need to be clarified: “adsorptive”, “adsorbent” and “adsorbate”. Since some of these terms are used synonymously depending on the source or language, the official IUPAC taxonomy will first be introduced. According to this, “adsorptive” refers to the free, still dissolved (guest) particles prior to adsorption, while the solid or interface to which it accumulates/concentrates is called the “adsorbent”. Once the adsorptive has accumulated (is adsorbed) at the corresponding interface of the adsorbent, it is also referred to as an “adsorbate” [114-116]. At this point, the terminology in German and the IUPAC nomenclature vary. In German, while “Adsorptiv” matches the IUPAC “adsorptive”, the term “Adsorpt” specifically refers to the species attached to the surface, whereas the complex formed from “Adsorpt” and adsorbent is called “Adsorbat” [112]. It should also be noted that, depending on the literature (in English), the term “adsorbate” is also used synonymously with “adsorptive” (e.g. in [113, 117]). This is probably because of possible difficulties to distinguish between the adjective and the noun in the English language. Therefore, in the following, this synonym use of the word “adsorbate” is also applied.

Various physicochemical processes can be involved in the actual adsorption process, whereby a first distinction is generally made between physical adsorption (physisorption) and chemical (chemisorption) adsorption. The distinction or classification is based on the type of interaction between the adsorbent and the adsorbate [112, 113].

In physisorption, the binding or enrichment of the adsorbate occurs via comparatively weak attractive forces such as Van der Waals or electrostatic forces and is therefore highly reversible. The nature of physisorption can be compared to condensation, but the driving force is primarily dictated by the properties of the adsorbate. A simple example would be the physisorption of noble gases at low temperatures, whereby an increase in temperature would shift the equilibrium towards desorption [112, 113].

Chemisorption is based on strong interactions between the adsorbent and the adsorbate, resulting in a strong chemical bond. The interaction at the interface therefore has the character of a chemical reaction, which can be either covalent or ionic in nature, although hydrogen bonds are also possible. The resulting bond is now significantly stronger than in the case of physisorption, which is why much harsher conditions are required to shift the equilibrium towards desorption. In chemisorption, the driving force of the adsorption process is determined by both the properties of the adsorbate and those of the adsorbent [112, 113].

To quantify the adsorption capacity or adsorption degree of the adsorbate on the adsorbent, the loading (q) is usually used. This quantity, usually expressed in $[\text{mg g}^{-1}]$, is defined as the amount of adsorbate per unit weight of solid/adsorbent at equilibrium. Depending on the adsorption kinetics, a maximum loading value or maximum loading capacity (q_{max}) can also be determined. This depends on several factors, such as the properties of the adsorbate and the adsorbent, the pH value, the temperature or even the pressure. Depending on the system investigated and the problem to solve, it can be necessary to determine the fractional coverage, which is defined as the ratio of occupied adsorption sites to the total number of available sites [112, 113, 118].

In a system with a constant temperature, it can generally be assumed that after a sufficiently long period of time, equilibrium will be established between the adsorbent, bound and free adsorbate (in solution). At this point, adsorption and desorption proceed at the same rate. In the case of gas-solid interface adsorption, this equilibrium depends on the partial pressure of the adsorbate in the gas phase. In the case of a liquid-solid interface, this dependence translates to the concentration of the adsorbate in solution. Such an equilibrium (at constant temperature) can then be expressed in the form of an isotherm, i.e. in the form of a mathematical function of the loading as a function of the partial pressure or concentration [112, 113].

According to Ghaedi [113], more than 100 different isotherms have been developed to date. These differ mainly in the type of interface (gas-solid, liquid-solid, etc.) and the various physical, mathematical or experimental principles or phenomena that are considered. As it would far exceed the scope of this work, only the three isotherms one should know will be discussed here: Henry, Freundlich and Langmuir isotherms. For those interested in learning more, including the thermodynamic principles, the book "Adsorption: Fundamental Processes and Applications" by Mehroang Ghaedi, published in 2021 is a good recommendation [113].

The Henry isotherm is the simplest of them all. It describes adsorption on a uniform surface at a relatively low adsorbate concentration and assumes that the density of the adsorbate is constant across the entire homogeneous surface. These assumptions result in Equation 2, which describes the linear relationship of the loading and the adsorbate concentration in solution (or partial pressure in the case of gases). There q is defined as above (loading in $[\text{mg g}^{-1}]$), C_{eq} $[\text{mg L}^{-1}]$ as the equilibrium concentration of the adsorbate/analyte in solution and K_{HE} is the Henry constant $[\text{L g}^{-1}]$ [113] (and references therein).

$$q = K_{\text{HE}} \cdot C_{\text{eq}} \quad (2)$$

Another fairly simple adsorption isotherm that is nevertheless frequently used is the Langmuir isotherm. This assumes a reversible adsorption process of a single layer of adsorbate, whereby the adsorption enthalpy of all adsorbates is the same, regardless of their state and adsorption situation. In other words, the Langmuir isotherm is based on the assumptions that adsorption takes place at energetically equivalent sorption sites, that the maximum amount of bound adsorbate cannot exceed the available sorption sites, and that there is no interaction between the adsorbates. From the second assumption, it can therefore be deduced that Langmuir assumes the formation of a monolayer. Equation 3 shows the mathematical formula of the Langmuir model. K_L [L mg^{-1}] is the Langmuir coefficient and $q_{\max}$ [mg g^{-1}] is the maximum loading capacity, i.e. the maximum amount of adsorbate that the adsorbent can absorb [12, 113, 119, 120].

$$q = q_{\max} \cdot \frac{K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \quad (3)$$

The next simple but equally frequently used model is the Freundlich isotherm. Contrary to Langmuir, this model assumes multi-layer adsorption on heterogeneous surfaces, i.e. at sorption sites of different strength and energy. Thereby adsorption energy increases exponentially with the number of available adsorption sites. However, this also means that the stronger sorption sites are occupied first and the binding strength decreases as the degree of occupation increases. Furthermore, Freundlich's model also accounts the interaction between solute species and an uneven distribution of adsorption heat across the surface. In contrast to the Langmuir isotherm, however, no $q_{\max}$ is defined here, which is why Freundlich's model is more suitable for questions involving low to medium concentration ranges [12, 113, 121-123].

$$q = K_F \cdot C_{eq}^{\frac{1}{n_F}} \quad (4.1)$$

$$q = K_F \cdot C_{eq}^n \quad (4.2)$$

Equation 4.1 shows the most common mathematical form of the Freundlich isotherms, which is also derived from the form postulated by Herbert Freundlich in 1907 [121, 124]. Here, K_F [L mg^{-1}] is the Freundlich coefficient and n_F is the Freundlich exponent [113, 121, 122, 124]. However, there are also other representations in the literature, including the form shown in Equation 4.2 [12, 56, 123, 125]. The two differ only in the expression in the exponent: $\frac{1}{n_F}$ or n . Thus, $\frac{1}{n_F} = n$ also applies, this distinction is often irrelevant, as the exponent, i.e. " $\frac{1}{n_F}$ " or n , is usually discussed as a whole [113, 125]. Even Freundlich, for example, mentioned and discussed the exponent, at that time " $\frac{1}{p}$ ", as a whole in his 1907 publication "Ueber Kolloidfällung und Adsorption" [124]. In short, it is irrelevant whether Equation 4.1 or 4.2 is used; care must only be taken to ensure that the variables are clearly defined.

To determine adsorption isotherms of specific adsorbates/analytes on the selected adsorbent, usually, batch experiments are conducted. In these experiments, several solutions with the same volume and increasing analyte concentrations are equilibrated with the selected adsorbent (always the same mass) over a defined period of time (at the same temperature) until equilibrium is reached. The concentration of the analyte in the supernatant solution (C_{eq}) is then determined, from which the retention (e.g. R_d in Equation 7.1 and 7.2) and q can be calculated (if the adsorbent mass is known). If q is then plotted against C_{eq} , the parameters of the various isotherms can be fitted [37, 113, 126, 127]. Albeit batch experiments are the most used, they suffer from various problems: For most the unrealistic solid to liquid ratios, which, in the context of the repository research, is more like an approximation of natural conditions and can be questioned regarding representation. Moreso batch experiments are regarded as static, meaning that the experimental time is set in a way that an equilibrium is reached. Unfortunately, this is often not even monitored or checked – 7 d is a usual time span [12, 128-131].

Sorption experiments can now be carried out not only in batch, but also dynamically using fixed bed column experiments (FBCE), as described in the column experiments in Chapters 3.1.2 and 3.1.3. In general, column experiments can be understood as the dynamic alternative to batch experiments. Since column experiments do not necessarily involve a constant volume or, in the case of leaching, a constant adsorbent mass, and since it cannot necessarily be assumed that an equilibrium state ever establishes (dynamic conditions), it is questionable whether the isotherms described can be applied universally to column experiments. Consequently, fixed bed models are typically preferred for evaluating column experiments [113, 117, 132, 133].

In fixed bed experiments, the adsorbent is packed into a column and the eluent containing the adsorbate/analyte is pumped through it either from top to bottom or from bottom to top. A quantitative evaluation of such FBCEs is performed using breakthrough curves (BTC). Figure 10 shows a schematic representation of the typical BTC over the course of a FBCE. There C_0 is the initial concentration of the adsorbate/analyte in the eluent and C_{eq} is the corresponding concentration in the eluate (after the column). When the eluent with the analyte concentration C_0 hits the "fresh" column/adsorbent, the mass transfer zone (MTZ) forms at the column inlet (light blue in Figure 10). The MTZ describes the part of the column bed in which adsorption takes place and thus also initiates saturation. At the first point in Figure 10, the adsorbent can remove/adsorb the entire analyte from the solution. The eluate does not contain any analyte (C_1) and $\frac{C_{eq}}{C_0}$ approaches 0. If the FBCE is continued and more analyte is continuously added to the column, the MTZ shifts further in the flow direction. The movement speed of the MTZ depends on many factors, such as the flow rate (Q), C_0 , the pH and the general properties of the adsorbent, such as porosity and adsorption capacity. Once the MTZ has advanced far enough, saturation gradually begins to set in (dark blue Figure 10). However, as long as the MTZ has not reached the end of the column, the concentration of the analyte in the eluate is still equal to C_1 and $\frac{C_{eq}}{C_0}$ still approaches 0. As soon as the MTZ reaches the end of the column, C_{eq} also begins to rise and the concentration of the analyte in the eluate is equal to C_2 ; this is the breakthrough point. From this point on, the MTZ becomes smaller and smaller, saturation increases, and C_{eq} , together with $\frac{C_{eq}}{C_0}$, rises steadily. At the end of the FBCE, the column is completely saturated, and no further

adsorption can take place. At this point, the analyte concentration in the eluate is equal to the initial concentration and the following applies: $C_{eq} = C_0$ or $\frac{C_{eq}}{C_0} = 1$ [113, 132].

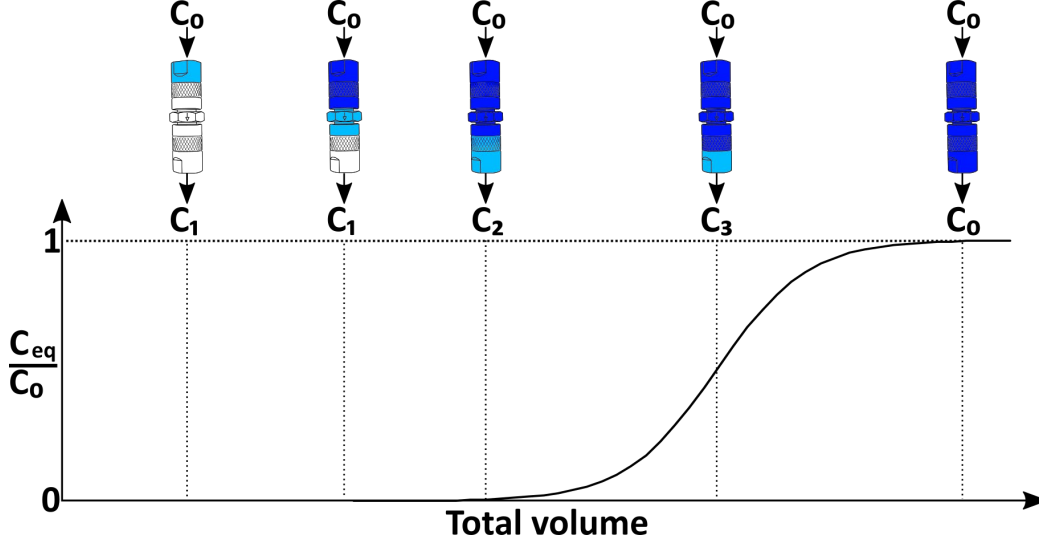


Figure 10: Ideal form of a breakthrough curve during a fixed bed column experiment (FBCE); light blue: mass transfer zone (MTZ); dark blue: saturated column volume; after Patel [132] and Ghaedi [113].

There are numerous ways to extract sorption parameters, and thus information about adsorbents and adsorbates, from the generated BTC; if interested, see Ghaedi [113] or Patel [132]. To discuss all of these would again go beyond the scope of this work, which is why only the option that is applicable to the question under investigation and was also applied will be discussed: the Thomas model. The Thomas model is a relatively simple approach to fit a BTC, but it is also the best understood and most frequently used model, which is why it was also used to fit the BTC described in Chapter 3.1.2. In general, the Thomas model assumes reversible second-order Langmuir kinetics of adsorption and desorption, whereby axial dispersion can be neglected. This makes it ideal for FBCE with a constant flow rate. Equation 5 describes the Thomas model in the form used for the fits. Here, K_{TH} [$\text{mL mg}^{-1} \text{min}^{-1}$] is the Thomas constant, m [g] is the mass of the adsorbent in the column, C_0 [mg L^{-1}] the initial analyte concentration in the effluent and V_{Eff} [L] is the effluent volume [12, 113, 132-139].

$$\frac{C_{eq}}{C_0} = \frac{1}{1 + \exp \left[\frac{K_{TH}}{Q} \cdot (q_{max} \cdot m - C_0 \cdot V_{Eff}) \right]} \quad (5)$$

As mentioned at the beginning of this chapter, many factors must be considered when modelling a potential repository system. For example, the nature of the medium in the near field of the repository (e.g. porewater) has a significant influence on the overall retention behaviour of the radionuclides. Depending on the pH or ionic strength, radionuclides can adsorb, precipitate or complex (e.g., see Chapter 2.6). However, co-precipitation of two different radionuclides is also conceivable, or competitive reactions for adsorption sites may occur between different adsorbates and adsorbents. In short, it is often difficult to distinguish between the various interaction processes and retention phenomena, particularly in the case of repository research. For this reason, it is common praxis to define the total retention R [%] (Equation 6) and/or the retention distribution ratio R_d (also known as K_d) [$L\ kg^{-1}$] (e.g. see [12, 16, 34, 39, 140, 141]). The latter is often also given in logarithmic form as $\log(R_d)$.

$$R = \frac{C_0 - C_{eq}}{C_0} \cdot 100\% \quad (6)$$

The R_d value is described as shown in Equation 7.1 but can be simplified as shown in Equation 7.2 – so done in the publication shown in Chapter 3.1.2 [12]. The parameter V [L] represents the volume of the background electrolyte, m [kg] the mass of the adsorbent, q [$mg\ kg^{-1}$] the loading of the analyte onto the adsorbent.

$$R_d = \frac{C_0 - C_{eq}}{C_{eq}} \cdot \frac{V}{m} \quad (7.1)$$

$$R_d = \frac{q}{C_{eq}} \quad (7.2)$$

2.6 Repository Relevant Elements

Considering the circumstances described, in connection with a potential repository, it must be expected that, at a certain point in time, radionuclides may migrate into the near field of the final repository. It is therefore of utmost importance for the safety assessment of a final disposal site to determine the extent to which these radionuclides interact with the surrounding construction and backfill materials in the near field. For this reason, numerous studies have been and continue to be conducted to investigate these interactions with potential materials for geotechnical barriers in model systems, including C-S-H phases, as described below. Since it is virtually impossible to represent all potentially migrating elements/radionuclides in a single experiment or study, a selection must be made. For the present work, the repository relevant elements Mo(VI), Cs(I), Sm(III), Eu(III), and U(VI), were selected.

2.6.1 Uranium

Alongside thorium and plutonium, uranium is probably the best-known representative of the actinide group (An) and, like all An elements, is radioactive. However, of all known An elements, only uranium and thorium occur in significant quantities in nature. Due to the high reactivity of all An elements, they are never found in their pure form, but always as chemical compounds—often as oxides. The first (deliberate) chemical conversion of such uranium ore was achieved by Martin Heinrich Klaproth in 1789. He reacted pitchblende (U_3O_8) with a strong acid and obtained a black powder (UO_2). Mistakenly assuming that he had discovered a new element, he named it uranium – after the planet Uranus, which had been discovered shortly before. It was not until Eugène-Melchior Péligot succeeded in producing pure uranium from the reaction of UCl_4 with potassium. This was followed by the establishment of uranium in industry, e.g., for coloring glass, and later, as described at the beginning, the discovery of radioactivity by Becquerel in 1896 [26] (and references therein).

Both the chemical and physical properties of uranium and its compounds are described in a concise but very clear manner in Hermann Sicius' textbook "Handbuch der chemischen Elemente" (Handbook of Chemical Elements) published in 2023 [26]. However, due to the focus of this work, the main emphasis should be placed solely on the primary application of uranium: its use as a nuclear fuel. All naturally occurring uranium isotopes (^{234}U , ^{235}U , and ^{238}U) are alpha emitters but of these, the isotope ^{235}U , as the most efficient fissionable material, is used for this purpose. ^{235}U has a half-life of $703.8 \cdot 10^6$ years and is parent nuclide for the natural uranium-actinium decay series (see Figure 11). However, ^{235}U only occurs at 0.7 wt.% in natural uranium, so it must be enriched for nuclear use [26]. A distinction is generally made between low-enriched uranium (LEU) and highly enriched uranium (HEU). The boundary between the two is drawn at a ^{235}U content of 20%. Whereas LEU is primarily used in nuclear power plants, HEU is primarily used for research purposes, in medicine, and also for the construction of nuclear weapons [26, 27]. According to Hermann Sicius [26], 210 MeV are released when an atom is split. In a modern nuclear power plant, depending on the type of reactor and a 90% conversion to thermal energy, this results in an output of 36 to 56 MWh per 1 kg of naturally occurring uranium [26].

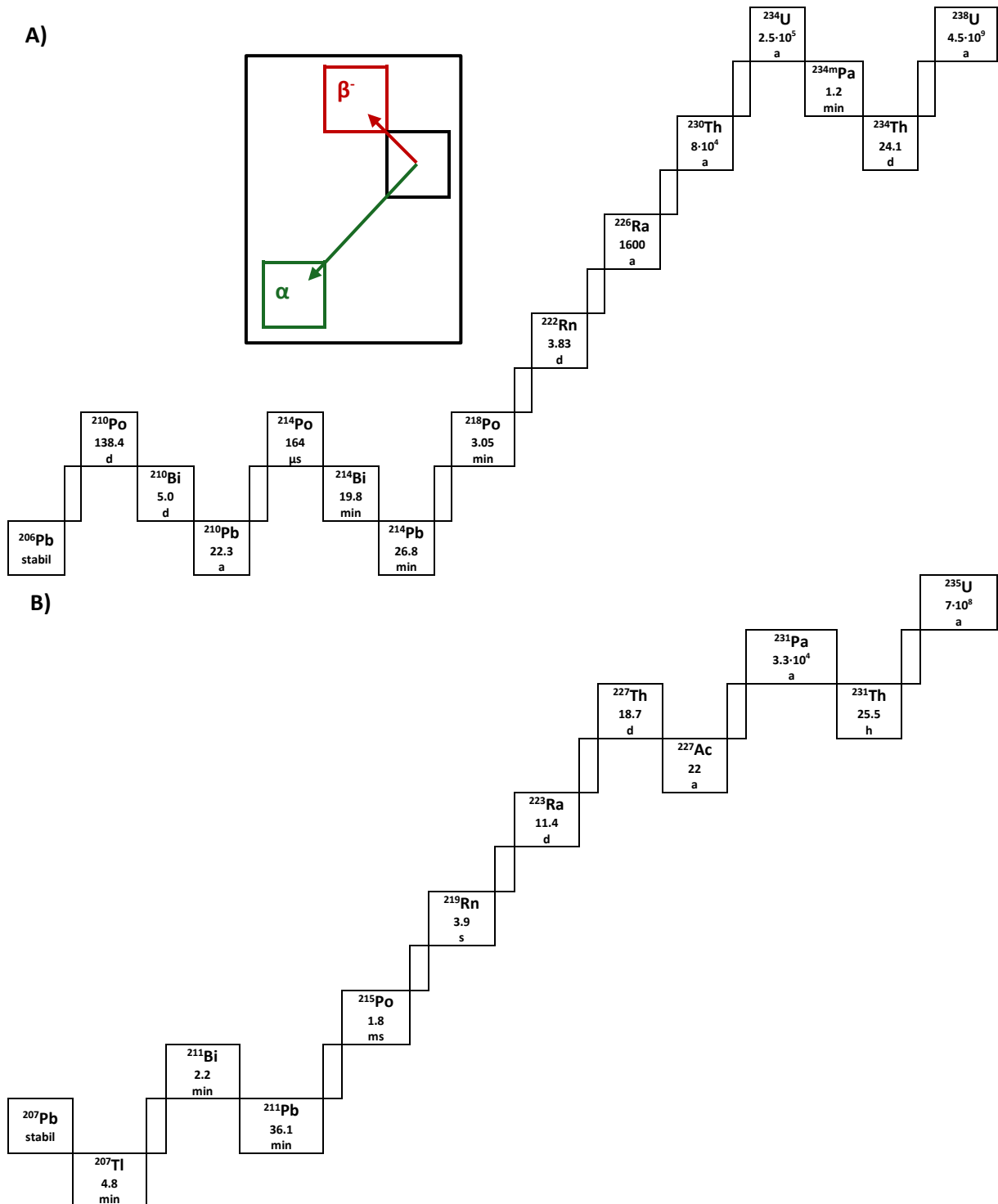
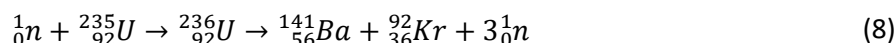


Figure 11: Scheme of A) decay chain of ^{238}U (also known as the Uranium series; $A = 4n + 2$) and B) decay chain of ^{235}U (also known as the Actinium series; $A = 4n + 3$); after Scholz [142].

Heavier atoms such as ^{235}U , with a binding energy of approximately 7.6 MeV per nucleon, tend to decay easily into elements with different masses but higher binding energies [28]. Figure 11 shows both, the decay chain of ^{238}U (Uranium series) and the one of ^{235}U (Actinium series) [142]. In this context, it has been observed that when ^{235}U absorbs a neutron, it immediately decays into the following products [28]:



Equation 8 shows that the capture of one neutron results in the release of 3 neutrons, which in turn causes a chain reaction. As mentioned in Chapter 2.1, this was also the reaction that resulted ultimately in the utilisation of spontaneously triggered fission. Unfortunately, the first technical application of nuclear fission was in a destructive nature and resulted in the destruction of Hiroshima and Nagasaki by the U.S. military. But thereafter, however, it was realised that the released neutrons could be controlled, which led to the development of the first nuclear reactors. The two established designs of these are gas-cooled reactors, in which graphite is used as a moderator, and deuterium reactors (heavy water reactors), in which heavy water serves as both a coolant and a moderator. Those moderators serve to control nuclear reactions by slowing down the released neutrons. The slower neutrons obtained increase the adsorption cross section of ^{235}U and the reaction in Equation 8 proceeds favourably. In addition, boron is often used as an efficient neutron absorber to better control the balance between the fusions taking place and the neutrons released [28].

Since uranium, e.g., as UO_2 , is the main component of nuclear fuel [28, 29], it is also of central importance for providing safety assessment for a potential HLW repository. For example, uranium is also listed as a long-term relevant radionuclide in the above-mentioned StandAG of the Federal Republic of Germany [10]. Therefore, the following section briefly discusses the key aspects of uranium in the near field of a potential repository, focusing on interactions with C-S-H phases.

In the near field of a potential HLW repository, uranium is mainly expected to occur in the oxidation states +IV and +VI [33, 141]. But, in contact with C-S-H phases uranium primarily exists in the oxidation state +VI [8, 30-32]. In general, many studies have observed high U(VI)-retention on cementitious materials – mainly via precipitation, incorporation, direct surface complexation or a ternary Ca(II) uranate-like surface precipitates [19, 31, 34-43]. Regarding surface adsorption, it was postulated that U(VI) forms mono- and bidentate outer-sphere UO_2^{2+} complexes on the C-S-H surface, which are bound to deprotonated oxygen atoms of the bridge Si(IV) tetrahedra. Since Ca^{2+} can occupy the same sites, competition between UO_2^{2+} and Ca^{2+} is suspected [30, 40, 42]. In general, the chemistry of uranium in aqueous solutions is difficult to describe due to the many possible chemical species. As mentioned in Chapter 2.3 and 2.4, due to cement alteration high pH values are to be expected in the near field of the repository. To better estimate the relevant U(VI) species, Figure 12 shows the speciation diagram of U(VI) in the pH range from 5 to 14. To substantiate the distribution shown there, references from the literature that also deal with the speciation of U(VI) can be consulted. Two of these are particularly noteworthy, especially in the context of the repository research: Brix et al. [141] and Schmeide et al.

[140]. Brix et al. [141] present different speciation distributions, whereby the atmospheric and aquatic conditions were varied. Among other things, a distribution under conditions almost identical to those in Figure 12 can be found there (in their supplementary data). It is therefore not surprising that both cases (Figure 12 and Brix et al. [141]) show hardly any significant differences, whereby in each case negatively charged uranyl hydroxide species dominate at a pH > 9. Furthermore, Brix et al. [141] – again in the supplementary information – presented another speciation distribution also in 0.1 M NaCl, but under atmospheric conditions, where the speciation is dominated by $\text{UO}_2(\text{CO}_3)_3^{4-}$ in the pH range of 8–12 [141]. Schmeide et al. [140] presented a quite similar speciation distribution (pH 8.5–13), but with the difference that their modelling considers the presence of C-S-H phases. There are hardly any differences to Figure 12, with only one being noteworthy: at a pH < 9.5, U(VI) speciation is dominated (up to approx. 70% at pH = 8.5) by $\text{UO}_2(\text{SiO}(\text{OH})_3)^+$ [140].

As can be seen in Figure 12 (representative for most speciation diagrams from literature), at a pH > 10, U(VI) is only present as a negative species, which generally counteracts adsorption on negative surfaces. In this context it is interesting to mention that in connection with C-S-H phases, increased retention was observed at higher C/S ratios. As a result, it was postulated that Ca^{2+} ions from the C-S-H must be involved in the retention mechanism of U(VI) [15, 16, 30, 34, 41].

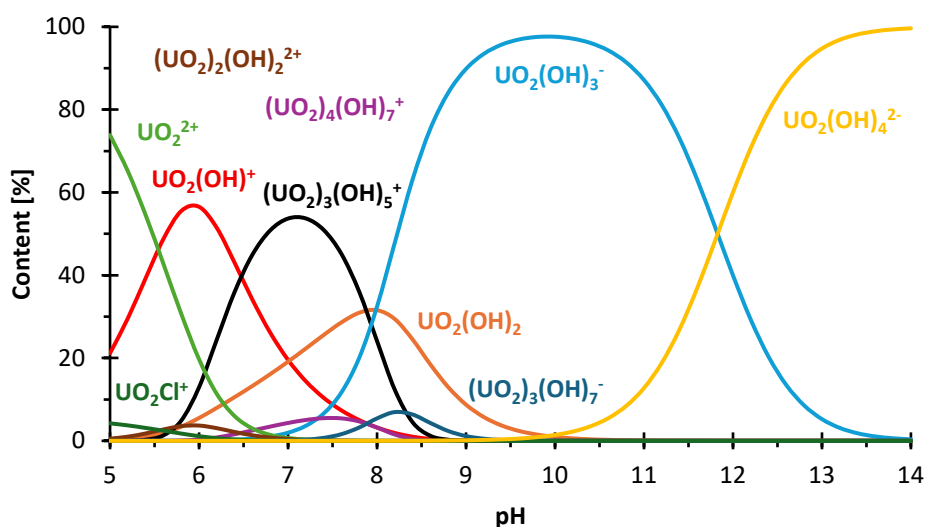


Figure 12: Speciation diagram of U(VI) in water; with $C(\text{U}) = 5 \cdot 10^{-7} \text{ mol L}^{-1}$, $I = 0.1 \text{ M NaCl}$ and $p(\text{CO}_2) = 0$; calculation with PHREEQC (Version 3) using Thermochimie database (Version 11a; PHREEQC_eDH_e_ThermoChimie_v11a) [143, 144].

Since the ingress of porewater is to be expected in a potential repository in deep geological rock formations (see e.g. Eisenbud et al. [45] and Jobmann et al. [11]), the remobilisation of bound uranium should also be investigated to provide valid safety assessment. Regarding the remobilisation of U(VI) from C-S-H phases, studies have shown that a lower pH value and the presence of CO_3^{2-} can increase the release of U(VI) due to the formation of soluble U(VI) species. Furthermore, it has been postulated that increased ionic strength affects the structural integrity of the C-S-H phases, but has no or only a negligible influence on the remobilisation of U(VI) from these phases [8, 30, 140]. The latter should be

reconsidered, especially in light of the results shown in Chapter 3.1.3. There, it is shown that the remobilisation of U(VI) from C-S-H phases may well depend, at least to a small extent, on the ionic strength of the surrounding porewater [8].

2.6.2 Caesium

In 1861, Robert Wilhelm Eberhard Bunsen and Gustav Robert Kirchhoff examined spring water in Bad Dürkheim for possible separations of the elements Li, Mg, Ca, and Sr. They found that after a complete separation, two unknown elements still remained in the filtrate. Due to the unknown blue spectral lines of one of those, they named it caesium (Cs), after the Latin word “caeruleum” for sky blue. Cs is extremely reactive and therefore occurs naturally only in the form of minerals, but is with an abundance of approx. 3 ppm in the earth's crust the rarest alkali metal after Fr [55] (and references therein). Although Cs can be classified as relatively harmless to mammals and occurs in nature only as the non-radioactive mononuclidic element ^{133}Cs , it is nevertheless relevant for the safety assessment of a potential repository. Among the artificially produced Cs isotopes, ^{137}Cs is the most important in this context. It is produced as a fission product in nuclear reactors and is itself a beta emitter with a half-life of approximately 30 years [2, 29, 54, 55]. The reactor accident in Chernobyl is a numerical example of its relevance for nuclear facilities. As a result, the radiation released by ^{137}Cs alone amounted to $8.5 \cdot 10^{16}$ Bq, and even in Western Europe, an increased accumulation of ^{137}Cs was detected in mushrooms [55, 145]. For this reason, it should be no surprise that Cs is also listed in the StandAG as a long-term relevant radionuclide [10].

Regarding the Cs retention on cement-based materials, many studies have already been published [16, 19, 34]. One work that deserves a special mention is the review article by Nicholas D.M. Evans from 2008 [19], which describes the Cs(I) retention mechanisms known at that time in cement-based materials, and particularly in C-S-H phases. It can be concluded from this that Cs(I) retention varies depending on the chemical composition of the cement. Regarding C-S-H phases, which contribute significantly to Cs(I) retention, the C/S ratio is decisive, regardless of the crystal structure. It is postulated that sorption occurs electrostatically at negatively charged sites in the C-S-H structure, with the silanol groups (Si-OH) being the presumed main point of attack. Further studies support this thesis by finding a high Cs(I) affinity to agglomerated silicate particles [19] (and references therein). Furthermore, it has been reported that Cs(I) retention decreased significantly with increasing C/S ratio [63]. Unlike uranium, anticipating the aqueous Cs species is quite simple: Cs does not precipitate over a wide pH range (according to Hakem et al. [56] between 2 and 14) and is most likely only present as dissolved Cs^+ , so that C-S-H phases can primarily be expected to act as a retention mechanism through sorption or incorporation [12, 34, 56, 57]. This assumption is also confirmed by further literature: depending on the study, either ion exchange reactions, inner or outer sphere complexes are reported, whereby all three may also be involved [34, 58-61, 63].

2.6.3 Europium and Samarium

Like other rare earth elements (REE), due to its high reactivity (the highest among all lanthanides) europium (Eu) only occurs in the form of minerals. Furthermore, all REEs are chemically very similar, so they tend to be found not in isolation but as mixed compounds. Thus, the first historical reference to Eu was made in 1885 by Sir William Crookes when he noticed unknown orange lines in the fluorescence spectrum of a samarium-yttrium mixed ore. He then postulated a new, unknown element, but was unable to identify it. It was not until 1901 that Eugène-Anatole Demarçay who succeeded in isolating Eu by fractional crystallisation of samarium/europium magnesium nitrate double salts [146] (and references therein).

Eu is commonly used as a dopant in the manufacture of fluorescent (colouring) substances. These are used, for example, in screens or cathode ray tubes, but are also applied as a dye to euro banknotes to verify their authenticity [146] (and references therein). However, there is another area of application which is of greater interest for this work: Eu_2O_3 can be used in the control rods of nuclear reactors to increase the neutron capture cross section and was/is therefore widely used as such in reactors in the CIS states [146-148]. Similar to Mo, Eu, especially its isotopes $^{150\text{m}}\text{Eu}$, ^{152}Eu and ^{154}Eu , are defined by the IAEA as one of the relevant radionuclides in connection with the decommissioning/dismantling of nuclear facilities [44]. Although Eu itself would be relevant for the safety assessment, it is generally used in repository research primarily for another reason: Lanthanides have similar ionic radii to Am(III) and Cm(III), which are estimated in spent nuclear fuel, and are considered to behave also very similar in solution. Because of these chemical similarities, some are therefore often used as a less toxic and non-radioactive homologue, e.g. La(III), Sm(III) or Eu(III) [12, 29, 34, 45-48].

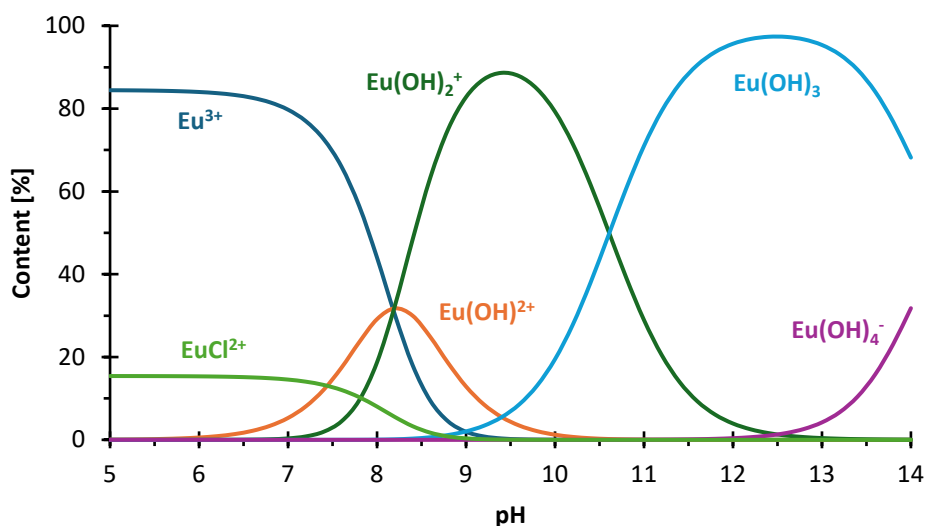


Figure 13: Speciation diagram of Eu(III) in water; with $C(\text{Eu}) = 5 \cdot 10^{-7} \text{ mol L}^{-1}$, $I = 0.1 \text{ M NaCl}$ and $p(\text{CO}_2) = 0$; calculation with PHREEQC (Version 3) using ThermoChimie database (Version 11a; PHREEQC_eDH_e- ThermoChimie_v11a) [143, 144].

As can be seen in Figure 13, Eu(III), similar to U(VI), has a rather complex speciation distribution. In the pH range relevant for C-S-H pore water, from approximately 11 to 14, $\text{Eu}(\text{OH})_3$ is the most dominant species and thus a neutral complex/precipitate. The work of Plancque et al. [149] can be used to support the calculation shown in Figure 13. It also contains a speciation analysis, although $\text{Eu}(\text{OH})_3(\text{aq})$ there dominates in the pH range from 10 to approx. 12.5, from where $\text{Eu}(\text{OH})_4^-$ becomes significantly more important (much earlier than in Figure 13) [149]. Since a neutral species dominates in the pH range of interest, electrostatic sorption sites would be considered as rather unlikely. However, the high affinity to OH^- ions intuitively suggests two retention mechanisms: the formation of C-S-H surface complexes and precipitation as hydroxide. The retention of Eu(III) in cement (phases) and especially in C-S-H phases has been well researched. The retention mechanism is described very well in the review article by Evans [19]. In it, he also cites the findings of Pointeau et al. [53]. They showed that Eu(III) is immobilised almost quantitatively (> 99.8%) by C-S-H phases, but contrary to the reasonable assumption, they were able to rule out precipitation as one of the retention mechanisms. Instead, they recognised that the C-S-H phases exert a strong attraction and thus dominate the retention mechanism. Through detailed spectroscopic analysis, they were able to identify two sorption sites: incorporation into the C-S-H structure through substitution of Ca and the formation of hydroxide surface complexes or -precipitates [53]. Those results were, in principle, corroborated Schlegel et al. [52]. Despite Eu(III) supersaturation, they were not able to observe the precipitation of pure $\text{Eu}(\text{OH})_3$ phases but proposed the formation of Si-Ca-Eu(III) secondary phases and were also able to identify Eu(III) sorption at the Ca sites [52]. These results, such as high retention, incorporation by substitution, and the formation of surface precipitates and complexes, are generally also reflected in other literature references. However, depending on the publication, more or less importance is attached to the formation of Si-Ca-Eu(III) (surface) precipitates [16, 34, 47, 50, 51, 150]. Also noteworthy is the study by Kee et al. [20], who synthesised C-S-H phases with very high Eu(III) addition (≥ 2.5 mol%), then examined them and observed a smaller particle size in the Eu(III)-C-S-H phases compared to those without Eu(III). In addition, with an Eu(III) addition of 20 mol% even a reflex shift of the tobermorite phase could be observed [20].

Due to the limited data available in the literature and, above all, due to the chemical similarity, Sm(III) will not be discussed in detail here. At this point, it is therefore assumed that everything described above for Eu(III) regarding the retention on C-S-H phases also applies to Sm(III). This decision is supported by the results in Chapter 3.1.1, whereby Sm(III) did not behave significantly different to Eu(III) [34].

2.6.4 Molybdenum

Molybdenum (Mo) is a relatively rare element, occurring at a concentration of approximately 14 ppm in the Earth's crust. Its most common natural form is molybdenite (MoS_2), which was first converted to MoO_3 in 1778 by Carl Wilhelm Scheele using HNO_3 . Peter Jacob Hjelm succeeded in producing pure metallic Mo in 1781 by reducing the latter with coal. Although it was long considered rather uninteresting, Mo is now a frequently used alloying element, for example to increase the strength of steel [151] (and references therein).

The isotope relevant for a repository safety assessment is ^{93}Mo , which is produced by neutron capture reactions of ^{92}Mo . Neutron capture occurs primarily in a variety of molybdenum-rich (steel) alloys used in nuclear power plant construction [66-69]. Molybdenum can also be part of the reactor fuel itself and is, more interestingly, usable as a potential material for nuclear fusion plants, where high neutron fluxes inevitably lead to the production of ^{93}Mo [64, 65, 69]. This is probably why the IAEA has defined ^{93}Mo and ^{99}Mo as important radionuclides in connection with the decommissioning of reactor facilities [44]. A half-life of 4000 years (with considerable uncertainty) was assumed for ^{93}Mo , whereas Kajan et al. [69] recently directly determined a half-life of 4839 ± 63 years [69, 152].

In the case of Mo speciation, the situation is similarly straightforward as with Cs. Although different oxidation states and chemical species are conceivable in principle, Pourbaix and speciation diagrams from the literature show that, in a repository-relevant Eh and pH range, only Mo(VI) in the form of MoO_4^{2-} is to be expected. Tapia et al. [70] present both types of diagrams (with unspecific aqueous conditions, such as Mo concentration). The speciation diagram shows that Mo is only present as MoO_4^{2-} at $\text{pH} > 6$. The Pourbaix diagram confirms this, whereas under strongly reductive conditions a MoO_2 phase would also be conceivable, which no longer occurs at a $\text{pH} > 8$ [70]. Another Pourbaix diagram can be found in Ochs et al. [13] ($C(\text{Mo}) = 10^{-8}$). In this, the limit is reached much earlier, so that at a $\text{pH} > 4$, the only possible species is the MoO_4^{2-} ion.

Regarding the immobilisation of Mo(VI) in/on cement-based materials, both the precipitation of powellite (CaMoO_4) and substitution in AFm phases have been reported [19, 74, 153]. More important towards the role of C-S-H Phases: In a previous study Lange et al. [71] demonstrated a significant contribution of C-S-H phases to the total Mo(VI) retention in Portland cement. However, Grambow et al. [72] compared the results of different studies towards the retention on C-S-H phases and came to the same conclusion but had to note negatively that the results varied greatly. Regarding the mechanism it was also suggested that a higher C/S ratio results in a higher Mo(VI) retention. In this context an electrostatic sorption on the positive C-S-H surface ($C/S \geq 1.2$; see Chapter 2.4) was postulated. Thereby, significantly lower retention was observed in alkali-rich cement pore water, which in turn was associated with a strong pH influence: OH^- and MoO_4^{2-} compete for these sorption sites on the positive surface [71, 72]. In another study by Caselles et al. [74], Mo(VI) was added during C-S-H synthesis. Subsequent investigations showed no effect on the C-S-H structure, ruling out the incorporation of Mo(VI) into the mineral lattice. Despite the high C/S ratio of 1.6, it was therefore postulated that the retention-determining mechanism was probably precipitation as CaMoO_4 , whereby adsorption on the surface was not proven, but also not ruled out [74].

In summary, these findings suggest that the increase in Mo(VI) retention with increasing C/S ratio correlates strongly with Ca(II). Thereby, a larger amount of Ca(II) in the C-S-H structure increases the number of electrostatic sorption sites but also results in a higher Ca(II) concentration in solution, which in turn promotes the precipitation of CaMoO_4 .

2.7 Analytical Methods

2.7.1 HPLC and MCE

2.7.1.1 Chromatography and HPLC

The abbreviation HPLC stands for high-performance liquid chromatography, although the term high-pressure liquid chromatography is also widely used [154]. Before discussing the apparatus design and analytical methods, a general understanding of chromatography will be provided first.

Chromatography refers to a variety of different processes for separating substances. Similar to extraction, a substance X (the analyte) is transferred from phase X to phase Y. Unlike extraction, however, phase Y is stationary, i.e. it is held in place while phase X is continuously supplied and flows past phase Y. Phase X is called the mobile phase and phase Y is called the stationary phase. Regarding the mobile phase, a first distinction can already be made: It is either gaseous (gas chromatography, GC) or liquid (liquid chromatography, LC) [78, 155].

The basic principle of chromatography is the interaction of the analyte with the mobile and stationary phases. Let us now imagine two different analytes, A and B, which are in the mobile phase. The separation of these analytes then results from the strength of their interaction with the stationary phase and, accordingly, how they are retained as they flow through the experimental setup (more on this below). A further distinction can be made in the chromatographic separation method depending on the type of interaction of the analyte(s) with the stationary phase. The different types of chromatographic separation are shown in Figure 14 [78, 154, 155]. In adsorption chromatography, for example, the retention (retaining) of the analyte is determined by the degree of adsorption to the stationary phase, i.e. the more strongly the analyte adsorbs to it, the slower it flows through the experimental setup. As it is not directly relevant for this work, the other chromatographic separation methods shown in Figure 14 are not discussed further. However, if someone is interested, those are excellently described in Daniel C. Harris' book "Lehrbuch der instrumentellen Analyse" published in 2014 [78].

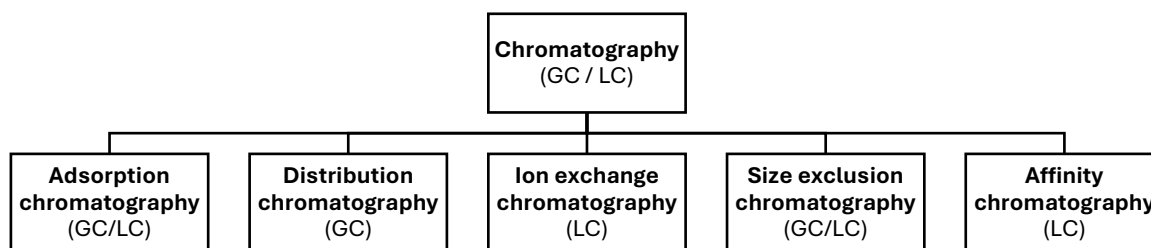


Figure 14: Differentiation of chromatographic separation methods according to the type of interaction between the analyte and the stationary phase; GC = gas chromatography and LC = liquid chromatography [78].

Since the methods used in this work are limited to LC, GC will be neglected from now on. The most prominent experimental setups in LC are thin-layer chromatography (TLC) and column chromatography. In TLC, the stationary phase is applied to a carrier plate [78, 154]. Silica gel (SiO_2) is most used for this

purpose, but Al_2O_3 or cellulose are also quite common [154]. The analysis solution is then dropped onto a “starting line”, and the chromatography carrier plate is placed in a vessel containing the mobile phase. The level of the mobile phase should be below the starting line. Due to the capillary action of the stationary phase, the mobile phase migrates upwards, and the substances are separated along the elution distance. Column chromatography is very similar to TLC, with the difference that the stationary phase is not applied to a carrier plate but is filled into a column and the mobile phase is actively pumped through the column. It should also be mentioned that, unlike in TLC, in column chromatography it is less concerned how far the analyte travels along the stationary phase but more how long it takes for it to leave the column again (see below; retention time) [78, 154].

One of the most used separation principles in LC is based on the different polarities of the mobile and stationary phases, whereby a distinction is again made between normal phase (NP) and reversed phase (RP) chromatography. In NP chromatography, a polar stationary phase is combined with a non-polar mobile phase, while the reverse combination applies in RP chromatography (hence the name). In both cases, the separation principle is based on the adsorption strength of the analyte to the stationary phase. The analyte is temporarily adsorbed to the stationary phase and gradually desorbed by the flowing mobile phase. In LC chromatography, the separation performance is adjusted by the selection of the mobile phase. For example, a polar analyte is retained stronger on a polar stationary phase in a strongly non-polar mobile phase than in a weakly non-polar mobile phase [154].

Now that the basic principles have been clarified, we will turn our attention to preparative methods, specifically HPLC as the most efficient form of column chromatography [155]. At this point, a brief note on the terminology used in LC column chromatography: the liquid entering the column is called the eluent, the liquid leaving the column is called the eluate (also known as the effluent), and the time while the liquid flows through the column is called elution [78].

Figure 15 shows the schematic drawing of a modern HPLC system on the right and an illustration of one of the systems used in this work (Agilent Infinity 1260 II) on the left (adapted from Gey [155]). Regarding the illustration, however, it should be noted that the actual module arrangement (pump, autosampler, etc.) may vary slightly. Back to the diagram in Figure 15: The eluent is in the storage bottles / solvent cabinet (a) and is pumped at high pressure towards the column/injector via a high-performance pump (b). In the case of the system used, this would be, for example, a quaternary pump with which pressures of up to 600 bar can be achieved. After the pump the injector (d) follows, or in modern systems, usually an autosampler. There, the analysis solution (c) is injected via a needle into a sample loop. Depending on the autosampler and sample loop, a wide range of possible injection volumes are possible. The sample loop of the setup used in this work has a total volume of 100 μL , allowing injections of 0.1–100 μL . The autosampler is followed by the guard column (e, optional) and the heart of the system, the (separation-) column (f). When a guard column is installed, it serves as a separation of possible contaminants and thus protect the main column. To increase the column lifetime, ideally, only the desired analytes should interact with the (separation-) column material. It is advisable that both columns are installed in a column oven, as been done for the adsorption column in this work, which ensures that the experiments are conducted at a constant temperature. To ultimately evaluate the separation, qualitative or quantitative analysis is then done using a detector (g) or several detectors (i,

optional) connected in series. The choice of detection always depends on the chemical and physical properties of the analytes to be detected. However, UV/VIS spectrophotometers, including diode array detectors (DAD), refractometer (RI) detectors, fluorescence spectrometers or mass spectrometric couplings (LC-MS or LC-ICP-MS, e.g. in Chapter 3.1.2), are most commonly used. Furthermore, if desired, a fraction collector (h) can be integrated into the experimental setup, which collects the eluate in defined fractions according to the individual conditions [155].

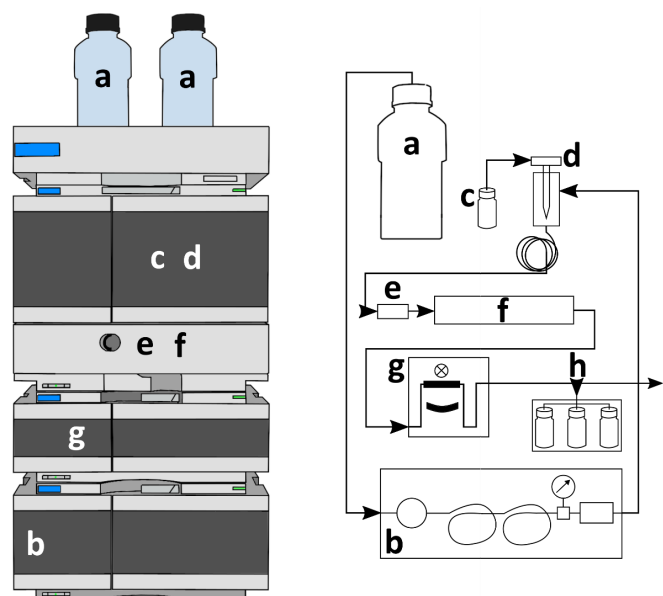


Figure 15: Left illustration (Agilent 1260 Infinity II) and right schematic representation of a modern HPLC (high-performance liquid chromatography) system with: a) eluent storage vessels/solvent cabinet, b) high-performance pump, c) analysis solution, d) injector/autosampler, e) guard column, f) main/separation column, g) detector (e.g., diode array detector; DAD), h) fraction collector, i) additional detectors or coupling with a mass spectrometer (MS or ICP-MS, see below); after Gey [155].

The result of separation using HPLC, but also using other column chromatography experimental setups, is a chromatogram, i.e. the plotting of the measurement signal against the elution time. If several analytes A, B and C are applied to the column with the eluent, and these are retarded differently on the stationary phase, they can also be recognised as different signals in the chromatogram. The theoretical chromatogram for this case is shown in Figure 16. It shows the signals of the analytes A, B and C with their respective retention times t_A , t_B and t_C . The retention time is the time that elapses from the injection (t_0) of the analysis solution to the detection of the respective analyte. In the example shown in Figure 16, it is assumed that analyte A does not interact with the stationary phase and passes through the column at the same speed as the mobile phase. Thus, t_A corresponds to the dead time (t_m) of the experimental setup. Since both t_B and t_C are greater than t_A and t_m , there is a retardation of analytes B and C at the stationary phase, with C being retained more strongly than B (since $t_C > t_B$). Figure 16 thus shows a successful separation of the three analytes. In such a context, the reduced retention time t' can also be specified. This is defined as the difference between the retention time and the dead time. For analyte B, for example, the following applies: $t'_B = t_B - t_m$, where $t_m = t_A$ [78, 155].

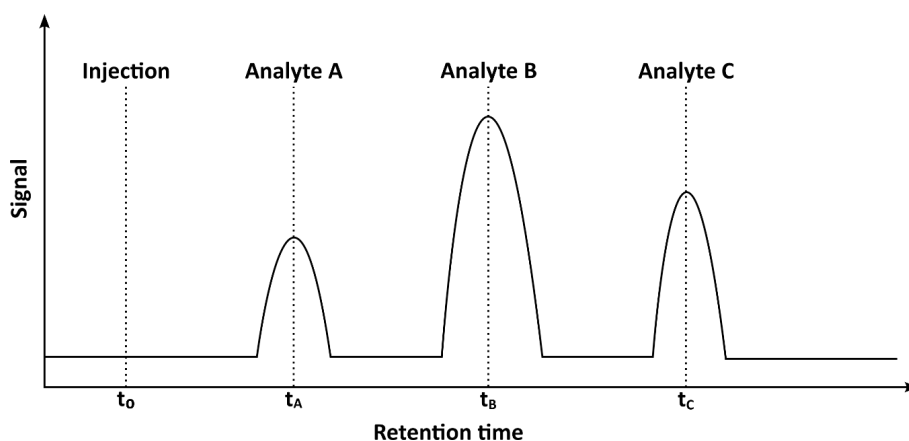


Figure 16: Example chromatogram of a column chromatographic separation of the three analytes A, B, and C with the corresponding retention times t_A , t_B , and t_C ; where $t_A = t_m$ with t_m = dead time; after Harris [78] and Gey [155].

In general, the separation efficiency of a column or experimental setup depends on several factors. These include, for example, the column length/floor height, the flow rate, the column diameter, and the properties of the column material/adsorbent, such as particle size. Since this work focuses less on separation efficiency and more on the general adsorption or retention capacity, the above parameters will not be discussed in detail. If one is interested, they are described well in the books by Harris [78], Ritgen [154] or Gey [155].

2.7.1.2 From FBCE to MCE

HPLC, which represents the most modern and efficient approach for (preparative) column chromatographic separation processes, has been explained in detail above. However, apart from chromatographic issues, columns are also used in connection with adsorption studies. One often used approach, as an alternative to batch experiments, are, as already described in Chapter 2.5, FBCEs. Another point that is often mentioned in connection with batch experiments is their time-consuming and resource-intensive nature [131, 156]. However, it should be noted that conventional column experiments cannot be described as entirely resource-efficient either. Examples for this can be found in the work of Li et al. [130] and Amiel et al. [157]. The former conducted column sorption experiments to investigate the retention of Cs on granite rock, focusing on the effects of the column length and the flow rate of the eluent (including analytes). As a starting argument, column experiments for determining retention parameters are described as time-consuming but are clearly the preferred method—especially in comparison to diffusion experiments, which take years to conduct. Therefore, the goal was to establish shorter columns. According to Li et al. [130], columns with an inner diameter (ID) of 2.5–7.5 cm and a length (L) of 2–200 cm are commonly used. In their work, columns measuring 5 x 2 cm (ID x L) and 5 x 8 cm (ID x L) were used, and flow rates of 1 and 5 mL min⁻¹ were employed [130] (and references therein). Under these experimental conditions, at least the resource-efficient aspect cannot be considered an advantage over batch experiments. The same applies to the work of Amiel et al. [157], who investigated the influence of humic acid on the transport behaviour of rare

earths in quartz sand using column experiments. They used columns measuring 3 x 19 cm (ID x L) and flow rates of 0.4 to 1.0 mL min⁻¹.

To eliminate the disadvantage of high material consumption in column experiments, the possibility of performing them using HPLC has emerged. A very good overview of different methods and approaches to determine adsorption isotherms for HPLC-based column experiments was published in the review article by Marchetti et al. [131]. In their work, they provide a state-of-the-art overview as of 2009, including the techniques Frontal Analysis (FA), Frontal Analysis by Characteristic Point (FACP), Elution by Characteristic Point (ECP), Perturbation Method (PM), and Inverse Method (IM). According to Marchetti et al. [131] the FA-approach is the most accurate and therefore most used one. FA can be performed either by immediate/abrupt changes in analyte concentration (single-step FA) or in staircase mode (staircase FA); but in both cases the analyte concentration remains constant until a plateau in the BTC is reached. In an single-step FA experiment, where the concentration in the eluent is abruptly changed only once, ultimately a BTC as described in Chapter 3.1.2 can be recorded [131]. This FA approach was, for example, also used by Li et al. [130] and Amiel et al. [157], but both did not derive isotherms from the generated BTCs. It is unknown if they could not do so or if it just was not in their scope. Like the name suggests, in a staircase FA, the analyte concentration is gradually increased, resulting in several breakthrough curves being recorded in succession. According to Marchetti et al. [131], from each BTC one point for q on the isotherm can be calculated, so that several BTCs (in series) are required to derive a complete adsorption isotherm. That means that either several single-step FA (with different analyte concentrations) or a staircase FA would have to be performed. This is where FACP and ECP offer an alternative. In both cases, the isotherm is derived from the rear end of the BTC (abrupt reduction in analyte concentration). However, according to Marchetti et al. [131], both approaches are significantly more error-prone and therefore, in case of doubt, also less precise; further details can be found in the review article.

Although, according to Marchetti et al. [131], the FA methods described are widely used, they have a major preparative disadvantage. When the analytes are continuously applied with the eluent, components of the HPLC system that are normally unaffected (such as eluent tubing, degassers, pumps, and several valves) can become contaminated with the analyte. It can therefore be assumed that it can get quite effortful to completely remove the analyte from the system, which can potentially result in intensive rinsing and cleaning procedures. One way to avoid this problem lies in the possibility of performing injection-based experiments. In this case, as usual for HPLC systems, the analyte would be injected into the eluent (via an injection loop) using the autosampler and thus transferred to the column. This approach would therefore be very similar to the IM method (and, in part, also the PM) described by Marchetti et al. [131], whereby in the case of repository research, it would be preferable to derive the retention parameters (isotherm) from the analyte concentration in the eluate rather than from the peak shape.

Particularly in relation to repository research, promising approaches for conducting injection-based and efficient column sorption experiments on HPLC systems have been developed in recent years. The idea is to fill miniaturised HPLC columns (usually HPLC guard columns) with the adsorption material of choice, inject the analyte via the HPLC-autosampler, and then quantify the analyte concentration in the

eluate (or in the solid), usually using inductively coupled plasma mass spectrometry (ICP-MS). Due to the small column size, this method is called mini-column experiments (MCE). Basic methodological approaches for performing MCE have already been published by Kautenburger [158], Sander [159] and Kautenburger et al. [129]. The MCE method was first presented in Kautenburger [158] – although at that time it was called MCCE (miniaturised clay column experiments). There, the method was presented as a link between insufficient natural batch techniques and extremely time-consuming diffusion experiments and used to investigate the migration behaviour of iodide, lactate, salicylate, and Eu(III) on clay materials and sea sand. Sander [159] adapted this idea and wanted to develop the MCE method in a way, that an easy routine method can be used to determine dynamic sorption parameters. In his work he performed MCE in two variants, injection-based and as frontal analyses, both as a possible online method in direct coupling with ICP-MS. Although rudimentary data analysis was successful, unfortunately, the implementation of a simple routine method (including convenient data evaluation) failed to materialise. In the publication by Kautenburger et al. [129], which also refers to the work of Sander [159], the MCE method was described as having been optimised to enable online quantification of the analyte in the eluate, thereby making the experimental setup even more efficient. The retention behaviour of Eu(III) on kaolinite and an opaline clay-sand mixture was investigated using the MCE method and MCE-ICP-MS coupling presented there. As a result, rudimentary quantification approaches were already possible, although the calculation of the retention parameters R_d (Equation 7.1 and 7.2), $q_{\max}$ (Equation 3 and 5) or the establishment of isotherms or other fits (e.g. Thomas model) was not possible [129, 159].

In principle, the MCE experimental setup allows extremely resource-efficient sorption experiments: depending on the adsorbent, experiments can be conducted with only approx. 50 mg of adsorbent and less than 100 mL of eluent. However, until the publication of Haben et al. [12] (Chapter 3.1.2), there was no valid MCE method for quantifying sorption processes and thus for calculating physicochemical sorption parameters. In Chapter 3.1.2 an MCE method for conducting sorption experiments of Cs(I) on C-S-H phases and of Eu(III) on kaolinite and quartz sand is shown. The data analysis presented there enables the calculation of dynamic sorption distribution ratios (R_d) and maximum loading capacities $q_{\max}$ [12] (and references therein).

As the latest evolutionary stage of MCE, the method has been adapted to enable the resource-efficient performance of leaching and remobilisation experiments. A manuscript on this topic has recently been published by Haben et al. [8], where the remobilisation behaviour of Si(IV), Ca(II), Mo(IV), Eu(III), and U(VI) from C-S-H phases was investigated (see Chapter 3.1.3).

2.7.2 ICP-MS and ICP-QQQ

To quantify the analyte content in supernatant solutions a powerful analytical method is required, especially in the trace range ($< 1 \mu\text{g L}^{-1}$). One of the most reliable and widely used methods for this purpose is ICP-MS. Since its commercial introduction in 1983, ICP-MS has become one of the leading techniques for (ultra-) trace element analysis in numerous matrices and various fields, such as geochemistry, the environment, clinical and biological materials, nuclear technology, the food and semiconductor industry [160, 161]. The main reason for this unparalleled dominance is undoubtedly its ability to perform rapid multi-element determinations in the ultra-trace range. Although in principle almost the same elements can be quantified as with other atomic spectroscopy techniques, such as flame atomic absorption (FAA) or inductively coupled plasma emission spectroscopy (ICP-OES), analysis using ICP-MS has clear advantages: It has excellent sensitivity and, at the same time, a large linear measurement range (sub-ppt to ppm), which in turn results in outstanding detection limits [161]. It allows rapid multi-element analyses and also the performance of isotope analyses [160, 161].

In general, the structure of a conventional ICP-MS can be roughly described using the following components/sections: sample introduction, nebuliser, spray chamber, plasma torch, ion focusing / ion optics, mass analyser and detector. However, the design of the interfaces between the components, the ion focusing system, the mass separation device, the vacuum chamber and also the detector can vary greatly depending on the manufacturer and field of application [161]. Two slightly different ICP-MS systems were used during this work: an Agilent 7500cx ICP-MS with a collision cell and an Agilent 8900 ICP-QQQ (triple quadrupole ICP-MS) with a collision/reaction cell. As the type designation suggests, the former is an older and therefore simpler system than the ICP-QQQ. The basic design of the 7500cx ICP-MS is quite similar to that taught in modern textbooks (e.g. Harris [78]). Therefore, the basic measuring principle will now be described using this system as an example.

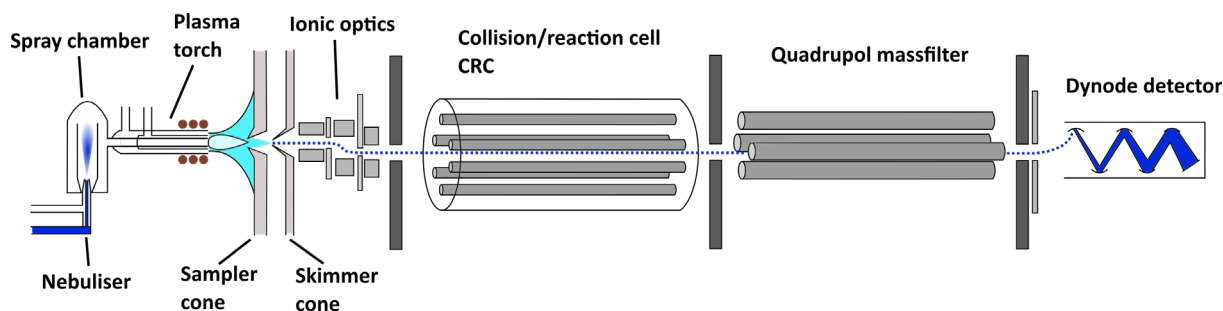


Figure 17: Schematic representation of a modern ICP-MS system based on the design of an Agilent 7500 ICP-MS; illustration adapted from / according to Agilent [162], Thomas [161] and Harris [78].

Figure 17 shows the schematic design of a modern ICP-MS system based on an Agilent 7500. The sample or analyte passes through the device arrangement from left to right. The (initially) liquid sample is usually pumped into a nebuliser using a peristaltic pump, where it is nebulised into a fine aerosol with the aid of argon gas flow (approx. 1 L min^{-1}). The nebuliser itself is in a spray chamber, which separates the large droplets from the small droplets of the aerosol formed. Only 1–2% of the droplets

formed in the aerosol leave the spray chamber as an ultra-fine aerosol and are transported to the plasma torch [161]. Regarding the design of the spray chamber, the double-pass spray chamber (Scott type), as shown in Figure 17, is the most used geometry – as is the case with the Agilent 7500 and 8900 devices. As an alternative, cyclonic spray chambers could also be used, although these are more commonly used in the field of ICP-OES applications [162, 163].

In the next component, the plasma torch, the substances dissolved in the sample are atomised and ionised [155]. The plasma torches used in commercial ICP-MS devices are usually based on the Fassel design [162]. In this design, the torch consists of three concentric quartz glass tubes, with the innermost tube carrying the sample aerosol, the middle tube carrying an auxiliary gas and the outer tube carrying the plasma/cooling gas. The plasma gas forms the plasma and also cools the torch, while the auxiliary gas primarily regulates the distance between the plasma and the torch, but also contributes to cooling [155, 162].

A radio frequency (RF) alternating current is applied to a copper coil surrounding the end of the torch. The oscillating magnetic field generated transfers (induces) the RF energy from the load coil to the atoms, thereby ionising the plasma gas (usually argon), which flows through the outer torch tube at a rate of approx. 15 L min^{-1} [161, 162]. According to Manfred Gey [155], alternating currents with a frequency of 40 Hz and a power of 900–1200 W are applied to generate the magnetic field. Depending on the application, however, frequencies of 27 Hz and powers of up to 1600 W are not uncommon in modern systems [162]. When the ionised gas is supplied with an electron source from a high-voltage spark, a plasma discharge with a very high temperature (approx. 10,000 K) occurs. After ignition, the Ar^+ ions in the plasma oscillate through the induced magnetic field with enough energy to ionise further argon atoms themselves, creating a stable plasma cloud at the end of the torch [155, 161-163].

The sample aerosol is then transported via a carrier gas (usually argon, from the nebulisation process) through the innermost tube of the torch into the plasma. There, the sample is desolvated, vaporised, atomised and finally ionised [162]. During this process, the atoms in the sample, ideally the analyte, are ionised by collisions with the oscillating Ar^+ ions or high-energy electrons. Since Ar has one of the highest ionisation energies at 15.8 eV – only He, Ne and F have higher energies – almost all known elements can be ionised in the plasma formed [78]. Most elements are present in the plasma as approximately 50–90% singly positively charged ions, although small proportions of doubly positively charged ions and simple molecules can also form [155]. The amount of unwanted doubly positively charged and molecular ions depends heavily on the conditions in the plasma. For example, a hotter plasma favours the formation of double charges, while a cooler plasma favours the formation of molecular ions [155, 162].

The transition between the plasma formed under atmospheric conditions and the high vacuum inside the ICP-MS device is provided by the interface. This consists of two pinhole apertures: the sample cone and the skimmer cone. Between these two is a pre-vacuum of approx. 1 Torr. When the plasma hits the water-cooled sample cone, an aperture usually made of Ni with a diameter of approx. 1 mm, the ion beam is accelerated or extracted towards the pre-vacuum and undergo initial focusing. The skimmer cone is located immediately behind the sampler (approx. 10 mm). This is also usually made of Ni and has a diameter of approx. 0.6 mm. The skimmer now forms the transition from the pre-vacuum to the

high vacuum (approx. 10^{-6} – $2 \cdot 10^{-5}$ Torr) [155, 161], whereby the ion beam is further focused and bundled in the direction of the ion optics [78, 155, 161, 162].

Behind the skimmer cone, in the high vacuum, at least in the case of the Agilent devices used, are the extraction lenses of the ion optics [162, 163]. The ion optics consist of several compact electrostatic lenses and apertures, which extract the ion beam from the interface area, thereby further focusing and accelerating it. Another important function here is to separate the positively charged ions from unwanted neutral particles, such as photons. This is necessary because neutral particles could pass through the mass analyser unhindered and thus cause high background noise at the detector [78, 155, 161, 162]. In the case of Agilent devices, highly transparent off-axis or omega lens arrangements are typically used, which separate the positively charged ions from the photons and neutral particles by applying a magnetic field that influences the cations in such a way that their trajectory in the ion optics describes an S-curve, thereby deflecting them from the axis of the original beam. Neutral particles, on the other hand, remain unaffected, do not describe an S-curve and collide with a metal plate, the photon stop [162].

Up to this point, the Agilent devices used (7500 and 8900) are nearly identical, except for minor generation-related differences, but differ in the following structure: While modern single quadrupole devices (hereinafter referred to as ICP-QMS) feature the collision/reaction cell (CRC) followed by the quadrupole mass filter, ICP-QQQ devices with double mass filters (MS/MS) feature a first quadrupole (Q1), then the CRC followed by a second quadrupole mass filter (Q2) [162, 164]. For a better understanding, we will continue with a description of the basic principle of an ICP-QMS using Figure 17 and will only later highlight the advantages of an ICP-QQQ (using Figure 18).

In addition to the desired single positively charged particles, doubly charged particles and molecular ions can also be produced in the plasma. There are several approaches to filter these unwanted interferences. The most widely used approach, and the one described in Figure 17, is a CRC before the actual quadrupole mass filter [78, 162, 163]. A small side note here: in the case of Agilent devices, the CRC is sometimes also referred to as an Octopole Reaction System (ORS) [162, 163]. This is a powerful means of removing isobaric interferences, i.e. interfering (molecular) ions with the same mass-to-charge ratio (m/z) as the analyte ion, from the ion beam. As the name suggests, filtering is based on collision or reaction. In the case of collision, a non-reactive collision gas such as He is introduced into the CRC. Multi-atom interfering ions now collide statistically more frequently with the He atoms and are consequently slowed down more strongly than analyte ions, so that the former, due to their now lower kinetic energy, can be selectively discriminated and thus filtered out [78, 162, 163]. In the case of a desired reaction, reactive gases such as H_2 , NH_3 , CH_4 , N_2O , CO or O_2 are introduced into the CRC instead of inert gases [78, 165]. Very clear examples are given in Harris [78] for both, collision cells and, in particular, reaction cells. The latter is discussed in more detail below in the description of the advantages of ICP-QQQ.

The CRC is followed by the heart of every ICP-MS: the mass filter. Possible mass filters include quadrupole, sector field and time-of-flight analysers (TOF). While quadrupoles achieve a resolution of approximately 400 and are therefore ideal for separating integer masses, sector field analysers achieve resolutions of approximately 10,000. These are therefore able to separate most isobaric interferences,

which are indistinguishable for a quadrupole. TOF analysers generally have lower sensitivity and less control over interferences than quadrupole and sector field spectrometers but are used for transient (time-resolved) applications due to their very high scanning speed. Of the types mentioned, however, the quadrupole is the most used analyser type in modern ICP-MS devices. The reasons for this include ease of use, robustness, the available mass range, high scanning speed and relatively low cost [162].

The quadrupole consists of four cylindrical metal rods (the electrodes), which are arranged in a square and parallel to the ion beam. The pairs of rods opposite each other are connected to a direct voltage, which in turn is superimposed by a high frequency voltage that is phase-shifted by 180 degrees [155, 162]. Depending on the ratio of frequency and amplitude of the alternating voltage (same voltage but phase-shifted between the two pairs) and the direct voltage (positive on one pair and negative on the other), different dynamic hyperbolic electric fields are generated [162]. These force the cations in the quadrupole into spiral trajectories, with each ion above or below the set m/z ratio enters an unstable flight path. The diameter of their spiral trajectory increases, causing them to strike the metal rods of the quadrupole and thus be removed from the ion beam. The combination of different alternating and direct voltages components thus results in a narrow-band filter that only allows a narrow m/z range to pass through [155, 162]. Since the set voltages can be varied very quickly, the m/z range can also be scanned very quickly, resulting in a mass spectrum for all elements and their isotopes (Li to U) being obtained quasi-simultaneously [162].

In both ICP-QMS and ICP-QQQ, the ions emerging from the (second) quadrupole must be converted into a measurable electrical signal. In most modern systems, dynode detectors, also known as electron multipliers or two-stage multipliers, are used. These consist of a series of discrete metal dynodes along the length of the detector (according to Gey [155] approx. 20). A high negative voltage is applied to the first dynode in this arrangement, so that all cations entering the detector are deflected or accelerated in its direction. When this ion strikes the dynode, several electrons are released from the dynode surface. Due to the high negative voltage, the released electrons are accelerated towards the second dynode, where they in turn knock out further electrons. This process is repeated along the dynode arrangement in the detector. When the electron cascade reaches the last dynode, the initial ion impact can be measured in the form of an electrical signal (as an electron pulse). This ensures reliable counting of a single ion [78, 155, 161, 162, 164]. Due to the choice of detector, very high dynamic ranges can be measured in modern ICP-MS systems [161]. For example, a report by Agilent shows a calibration curve of ^{115}In from 10 ppt to 1000 ppm [162]. This corresponds to a linear measuring range of 9 orders of magnitude. In another report, Agilent presents detection limits, with that of ^{238}U being approximately 1 ppq [164].

As already indicated above, there are scenarios in which isobaric interferences in the CRC cannot be filtered out by collision with an inert gas. In this case, chemical reactions in the CRC with the gases listed above can be exploited. The choice of cell gas depends on the interference to be eliminated. For example, H_2 is often used to eliminate interference, such as $^{40}\text{Ar}^+$ on $^{40}\text{Ca}^+$, $^{40}\text{Ar}^{12}\text{C}^+$ on $^{52}\text{Cr}^+$ or $^{40}\text{Ar}^{2+}$ on $^{80}\text{Se}^+$. In this case, only the ArM^+ interference reacts with the H_2 gas, ensuring an on-mass measurement (at the original element-specific mass). An example of a method using mass shift is O_2 as the cell gas. Here, O_2 reacts with the target analyte (M^+) to produce an oxide (MO^+). This method is used, for

example, in sulphur measurement. Here, $^{32}\text{S}^+$ reacts to form $^{32}\text{S}^{16}\text{O}^+$, and the quadrupole filters according to the m/z ratio of 48. Since the isobaric O_2^+ interference does not react with the cell gas, this mass shift method enables the targeted measurement of ^{32}S [165].

Both the H_2 and O_2 CRC methods can be performed with ICP-QMS and ICP-QQQ. However, the full potential of the various reaction modes often cannot be fully exploited with ICP-QMS. The problem here is that unwanted matrix elements can also react with the cell gas, which in turn can lead to further unwanted interference [165]. To overcome this limitation, ICP-QQQ systems have become established in recent years. The immense advantage of such an ICP-QQQ (compared to an ICP-QMS) is excellently illustrated in Agilent's technical overview from 2025 using the ^{80}Se measurement in O_2 reaction mode [164]:

Figure 18 A shows the measurement setup of an ICP-QMS analogous to Figure 17 – the CRC is located in front of the single quadrupole mass filter. Figure 18 B, on the other hand, shows the measurement setup of an ICP-QQQ, in which the CRC is preceded by a first quadrupole (Q1) and followed by a second quadrupole mass filter (Q2). In both cases, ICP-QMS and ICP-QQQ, $^{80}\text{Se}^+$ reacts with O_2 in the CRC to form $^{80}\text{Se}^{16}\text{O}^+$, which means that in both systems, the isobaric interference from doubly positively charged ions such as $^{160}\text{Gd}^{2+}$ or $^{160}\text{Dy}^{2+}$ and molecular ions such as $^{40}\text{Ar}_2^+$ can be filtered out by setting the target mass to $m/z = 96$ on the quadrupole behind the CRC. However, the ICP-QMS reaches its limits when the sample also contains elements with an m/z equal to the target mass ($m/z = 96$) that do not react (completely) with O_2 . These pass through the CRC and the quadrupole, resulting in a false high signal. However, if an additional quadrupole is placed in front of the CRC, these interferences can be eliminated using a mass shift method. Here, the m/z of the analyte, i.e. 80, is set at Q1. As a result, only the analyte ($^{80}\text{Se}^+$), the bivalent ($^{160}\text{Gd}^{2+}$ or $^{160}\text{Dy}^{2+}$) and the multi-atomic isobars ($^{40}\text{Ar}_2^+$) can pass through Q1; the interferences on the target mass ($^{96}\text{Zr}^+$, $^{96}\text{Mo}^+$ or $^{96}\text{Ru}^+$), however, cannot. From this point on, the system is the same as for an ICP-QMS method: only $^{80}\text{Se}^+$ reacts to form $^{80}\text{Se}^{16}\text{O}^+$, which can therefore pass through Q2 and is detected without interference [164].

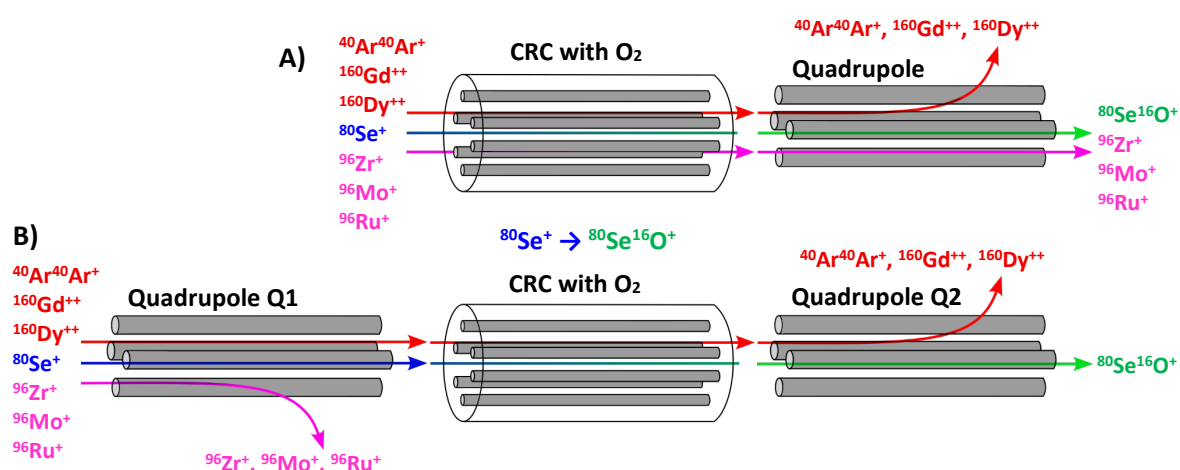


Figure 18: A) Conventional single quadrupole or bandpass ICP-QMS (ICP-QMS) and B) ICP-QQQ with double mass selection (MS/MS); after Agilent [164].

2.7.3 LA-ICP-MS

Laser ablation (LA) coupled with ICP-MS (LA-ICP-MS) is an established analytical method which, in addition to the direct quantification of major, minor and trace elements in solid samples, also enables the direct determination of isotope ratios in solid sample materials [77, 166, 167]. This method enables rapid, sensitive and powerful multi-elemental analysis at trace and ultra-trace levels (even in the ng g^{-1} range) with minimal sample preparation, making it one of the most versatile techniques for this problem/task [76, 166, 168].

The general design of LA has hardly changed in recent decades and still essentially follows the structure outlined in Figure 19 by Günther et al. [169].

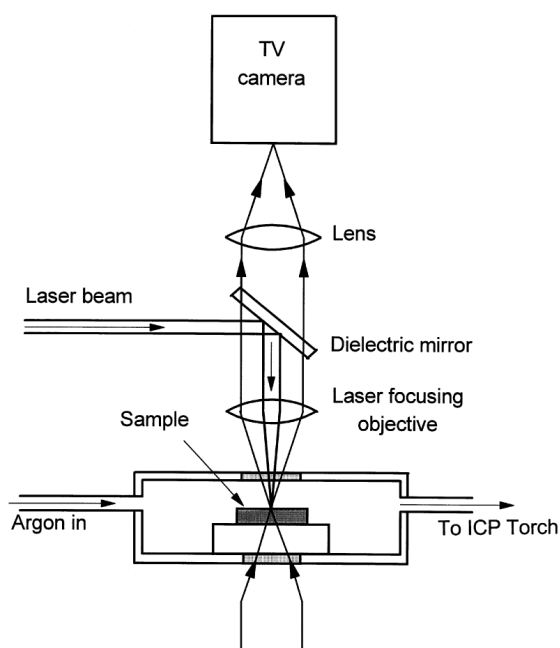


Figure 19: Schematic illustration of a laser ablation system by Günther et al. [169]; reprinted from *Spectrochimica Acta Part B: Atomic Spectroscopy*, 54, D. Günther, S.E. Jackson, H.P. Longerich, *Laser ablation and arc/spark solid sample introduction into inductively coupled plasma mass spectrometers*, 381-409, Copyright (1999), with permission from Elsevier [169].

First, the sample is transferred to an airtight ablation chamber, which is flushed with argon or helium - depending on the carrier gas in the subsequent analysis [77, 169, 170]. In this method, a pulsed laser beam (laser = Light Amplification by Stimulated Emission of Radiation) is focussed on a small area of a solid sample, whereby a spatial resolution of 1–100 μm is possible according to current standards [78, 169, 170]. In most cases, an Nd:YAG laser (neodymium-doped yttrium aluminium garnet laser) with a wavelength of 1,064 nm is used [78]. This output wavelength/basic harmonic of the Nd:YAG laser ($\lambda_1 = 1,064 \text{ nm}$) can then be converted into the second harmonic ($\lambda_2 = 532 \text{ nm}$), the third harmonic ($\lambda_3 = 355 \text{ nm}$), the fourth harmonic ($\lambda_4 = 266 \text{ nm}$), the fifth harmonic ($\lambda_5 = 213 \text{ nm}$) or even the sixth harmonic ($\lambda_6 = 177.3 \text{ nm}$) using non-linear optical crystals [171, 172]. In modern LA systems, however, a quintuple Nd:YAG laser with $\lambda_5 = 213 \text{ nm}$ is predominantly used [76, 168, 170, 173, 174] but the use

of excimer lasers with a wavelength of $\lambda = 193$ nm is also quite common [173, 175, 176]. The laser generates a pulse in the ns range with an energy of 0.01 to 100 mJ, depending on the application, which is then directed to a point with a previously selected diameter [78, 169, 175, 177]. For better comparability of the laser power, considering the spot size, the fluence [J cm^{-1}] is usually specified. For example, a laser power of 0.4 mJ would result in a fluence of 1 J cm^{-1} for an ablation spot measuring $20 \times 20 \text{ }\mu\text{m}$.

When the pulsed laser beam hits the sample, the sample is explosively transformed into the gas phase. The resulting aerosol consists of vapour, particles, agglomerates, atoms, ions and electrons [77, 78, 169, 170]. The material is usually removed to a depth of 0.02 to 5 μm with each pulse, which translates to ng quantities of the sample, meaning that the method can be considered almost non-destructive [78]. The sample aerosol generated in a closed chamber is then transported through a continuous gas stream (Ar or He) via a (PTFE-coated) tube to the coupled analyser (here ICP-QQQ) [77, 78, 169, 170]. Hence the name: “ablation” is derived from Latin and can be translated to “to carry away” [169]. In the Plasma, analogous to the liquid samples described in Chapter 2.7.2, the ablated material is evaporated, dissociated, atomised and ionised, what is followed by the quantification of the analytes according to their m/z ratio [77, 170, 178]. To determine depth profiles, successive pulses can also ablate the sample from deeper and deeper domains, allowing, for example, the chemical composition to be determined as a function of depth [78].

Despite the advantages, LA-ICP-MS analysis suffers from inherent challenges that make quantitative analysis difficult. The two most important ones are elemental fractionation and matrix effects [75, 77, 78, 167, 170]. Elemental fractionation refers to effects that occur during sampling, aerosol transport, evaporation, atomisation and ionisation in the plasma [77, 167, 170]. It manifests itself in non-stoichiometric signal ratios due to different physico-chemical properties of the elements (e.g. condensation temperature, first ionisation potential and evaporation enthalpy); for example, volatile elements are preferentially evaporated/ablated [167, 170, 178]. In other words, the relative number of ions detected does not necessarily correspond to the relative amounts of the respective analytes in the sample [78]. In general, element fractionation can be divided into time-, mass-, volatility- or matrix-dependent fractionation. For example, time-dependent fractionation results in temporal signal fluctuations during single-point ablation. Matrix-dependent fractionation, on the other hand, has its origin in different ablation performances of different sample matrices (more on this later) [170] (and references therein).

The element fractionation index is usually used to quantify element fractionation. This is defined as the ratio of the integrated and normalised signal obtained for the second half of a continuous ablation to the integrated and normalised signal for the first half (see Equation 9) [170, 178]. More information on this can be found in the original paper by Fryer et al. [179], as well as in the review articles by Lin et al. [178] and Yang et al. [170]. Alternatively, to the fractionation index/factor, the ratios of two representative elements with different volatilities, e.g. a volatile and a refractory element (e.g. Pb/U, Th/U, Pb/Sr), can also be used to assess the ablation behaviour. In this way, simplified approximate values are used for the evaluation of fractionation [170] (and references therein).

$$\text{Element fractionation index} = \frac{\frac{\text{Integrated signal analyte}_{\text{Second half}}}{\text{Integrated signal IS}_{\text{Second half}}}}{\frac{\text{Integrated signal analyte}_{\text{First half}}}{\text{Integrated signal IS}_{\text{First half}}}} \quad (9)$$

At this point, however, it should be noted that the efficiency of the laser ablation, and therefore also the element fractionation, is mainly dependent on the fluence, the pulse time and the wavelength of the laser, the ratio of depth to diameter of the crater formed and the composition of the matrix. Regarding these influencing factors, there are indications that, for example, the ratio of crater diameter to crater depth plays a far more important role than the laser wavelength. An important measure in counteracting fractionation is therefore to optimise the absorption of the laser light in the material. By using short wavelengths and laser pulses, as well as optimising the fluence, it can be ensured that well-defined craters with low penetration depths are produced. This means that the ablation parameters, and therefore the interaction of the laser with the sample material, must be optimised before the analysis in order to achieve a representative analysis results [75] (and references therein). For those who are interested: In two studies, Shaheen et al. [180, 181] investigated the interaction of laser pulses with different materials using scanning electron microscopy and thus provided visual examples of the relationship between energy density (fluence), the ablation performance and the spot/crater characteristics.

Like all quantification methods using ICP-MS/QQQ also the LA-ICP-MS is a relative analysis method, which is why matrix effects in particular must be considered (in addition to element fractionation). For example, differences in the physical properties between sample and calibration standard (e.g. absorption capacity, thermal conductivity, reflectivity, particle size, and geometry) lead to a different ablation yield; in other words, lead to different analyte masses ablated per laser pulse. Furthermore, depending on the matrix ablated, the aerosol particles generated can vary in size and geometry, which in turn leads to differences in sample transport from the ablation cell to the plasma. Since the ionisation efficiency in the plasma is strongly dependent on both, the quantity and nature of the materials introduced, these matrix effects are also directly related to this [75, 167, 176, 182].

To overcome the limitations described above (fractionation and matrix effects) and achieve accurate analysis results, a variety of different approaches for calibration strategies have been established over time. The most common ones are briefly presented here:

External calibration:

External calibration via matrix-matched standards, e.g. using certified reference materials (CRMs), is considered the most reliable method for accurate quantification [78, 167]. CRMs are available in a variety of different matrices, from NIST® glass standards (e.g. NIST® 612) to geological standards such as silicate and carbonate rocks, soils, sediments, ores, bio/minerals, etc. (e.g. Apatit Standard from the company "myStandards GmbH", Kiel, Germany) [75, 169, 183, 184]. Depending on the application, however, CRMs are not always commercially available, so that in many cases it is also necessary to use in-house produced reference materials (RM). Again, depending on the application, there are a variety of options. For inorganic materials, the most common preparation routines are the fusion of powdered

samples with, for example, borates to form homogeneous glass discs, or the production of nanoparticle compacts pellets. The latter are produced by wet grinding of sample powder into nanoparticles and subsequent pressing into pellets (see Chapter 3.2.1.1) [75, 167, 184].

A very elegant approach for quantifying trace elements in mussel shells was presented by Bellotto et al. [185]. These consist mainly of CaCO_3 . Therefore, to prepare the calibration standards, known quantities of the analytes (metals) were dissolved in an acidic solution with an excess of Ca^{2+} and then precipitated with CO_3^{2-} . The resulting carbonate precipitate was washed, dried and pressed into solid pellets. The results of the laser ablation were then compared with those after a complete digestion of the material and reference values and showed very good agreement (depending on the analytes) [78, 185].

Internal standardisation:

For the calibration method using internal standards (IS), elements of known concentration are added to the sample material (spiked). If used correctly, in this way effects such as sensitivity drift, differences in the mass removed and also a large part of the matrix effects can be corrected [75]. However, in addition to the known concentration of the IS, it must be ensured that the IS is homogeneously distributed in the sample and that it behaves analogously to the analyte(s) during ablation (keyword: element fractionation) [75, 167, 169]. If an IS is spiked, it must be ensured that it does not occur in the sample itself – ^{89}Y is often used. In addition to spiking an IS, an element that occurs in the sample itself can also be used. For biological samples, ^{13}C or ^{32}S is often used, while for geological samples any structuring element can be used (e.g. calcium in calcium-based materials) [75] (and references therein).

A fabulous addition to this technique is described in the review article by Miliszkiewicz et al. [75] ("summed spectrum normalisation"). Here, the sum of all signals of the (known) elements contained in the sample is used for normalisation, whereby the assumption is made that those signals represent the complete ablated mass. Using the relative signals of the analytes, a very fast semi-quantitative analysis can be conducted. However, if the analyte signals are considered as a function of the summed signals (entire sample matrix), signal fluctuations can be corrected in such a way that the LA-ICP-MS method is immune to matrix effects and thus significantly improves the precision of the analysis [75] (and references therein).

Solution-based calibration (solid-liquid calibration):

In a solution-based calibration, first introduced by Thompson et al. [186] as the "dual sample/standard approach", quantitative analyses are not performed with solid but aqueous standards [168, 186]. Here, the ablation aerosol is merged with an aerosol generated by nebulising an aqueous standard solution and introduced into the ICP-MS simultaneously. Technically, this "merging" is possible in several ways. It can be carried out using a one-gas flow system (nebuliser is inserted directly into the ablation chamber), a two-gas flow system (mixing takes place via a Y-piece) or, if the ICP-MS instrument has the appropriate equipment (see Chapter 3.2.1.2), directly on the ICP-MS device [75, 167, 168].

A very good approach for a solution-based calibration strategy was presented by O'Connor et al. [168]. They investigated the calibration strategy of the "dual sample/standard approach" and drew comparisons between the implementation under wet and dry plasma conditions. Crucially, however, they note that ablated particles have larger mean diameters and different size distributions than those produced by solvent nebulisation. These differences lead to deviating ionisation efficiencies in the plasma, which is why internal standardisation is essential for this method. The mass transport rates of the two sample introduction methods are then calculated using this standardisation, which ultimately enables quantification [168] (and sources within). The theoretical background and the analysis method are discussed in more detail in Chapter 3.2.1.2. Regarding plasma conditions, O'Connor et al. [168] concluded that a wet plasma is the preferred operating mode. This provided significantly more robust plasma conditions and thus ultimately more representative results.

Isotope dilution:

Isotope dilution (ID) is based on the measurement of the isotopic ratio of the analyte, which must not be monoisotopic. The isotope pattern is changed by spiking the sample with an isotopically enriched material. In this way, isotope-based internal standardisation takes place (as described, for example, in Michaliszyn et al. [76]). As only a different isotope of the desired analyte is used for calibration in the ID, it can be assumed that all interference factors (fractionation and matrix effects) are fully corrected, thus ensuring extremely accurate quantification [76] (and references therein).

3. Results and Publications

During the period of the doctorate, Aaron Haben contributed to a number of publications - sometimes in leading function as the first author, sometimes in a supporting role as second author, and sometimes as an additional co-author who performed analyses. All per reviewed publications are listed in Table 1.

Table 1: During the period of the doctorate (2022–2026), peer-reviewed publications.

K. Brix, A. Haben, R. Kautenburger, Time-Dependent Retention of a Mixture of Cs(I), Sm(III), Eu(III) and U(VI) as Waste Cocktail by Calcium Silicate Hydrate (C-S-H) Phases, <i>Minerals</i> , 2023 , 13, 1469.
K. Wissel, A. Haben, K. Küster, U. Starke, R. Kautenburger, W. Ensinger, O. Clemens, Direct Recycling of β -Li ₃ PS ₄ -Based All-Solid-State Li-Ion Batteries: Interactions of Electrode Materials and Electrolyte in a Dissolution-Based Separation Process, <i>Adv. Energy Sustainability Res.</i> , 2024 , 5, 2300280.
T. Rittner, J. Kim, A. Haben, R. Kautenburger, O. Janka, J. Kim, M. Gallei, One-pot Functionalization for the Preparation of Cobaltocene-Modified Redox-Responsive Porous Microparticles, <i>Chem. – Eur. J.</i> , 2024 , 30, e202402338.
T. Rittner, S. Pusse, B. Boßmann, K. Staudt, A. Haben, R. Kautenburger, H.P. Beck, M. Gallei, Metallopolymer-based block copolymers for perfluorinated substances (PFAS) and ion removal, <i>J. Mater. Chem. C</i> , 2024 , 12, 19116-19129.
A. Haben, K. Brix, N. Bachmann, R. Kautenburger, Sorption experiments as efficient as possible: Mini-column experiments (MCE) using HPLC-ICP-MS coupling with a new data analysis approach to determine sorption parameters, <i>Microchem. J.</i> , 2024 , 206, 111511.
M. Michak, T. Ruf, R. Denecke, C. Benndorf, A. Haben, R. Kautenburger, H. Kohlmann, Crystal chemical investigations on TiU ₈ S ₁₇ and U ₃₆ Lu ₂₁ S ₉₃ I ₃ - ordered and disordered multinary uranium sulfides, <i>J. Solid State Chem.</i> , 2024 , 340, 124998.
M. Jacob, H. Moreno Fernández, A. Haben, A.I. Waidha, S. Özel, J.P. Hofmann, R. Kautenburger, O. Clemens, K. Wissel, Direct Recycling of All-Solid-State Batteries with a Halide Solid Electrolyte via Water-Based Separation: Interactions of Electrode Materials in Aqueous Li ₃ InCl ₆ Solutions, <i>Batteries Supercaps.</i> , 2025 , n/a, 2500189.
C.L. Krämer, D.W. Müller, F. Arndt, A. Rehm, B. Walkenfort, A.S. Ahmed, A. Haben, A. Schiele1, A. Auerhammer, M. Hasenberg, A.L. Boschert, R. Kautenburger, S. Leuko, S. Janssen, M. Maurer, F. Mücklich, K. Siems, Touching Surfaces – Presence of Microorganisms on Antimicrobial Metal Surfaces on the International Space Station and in German Schools, <i>BMC Microbiol.</i> , 2025 , 25, 631.
F. Arndt, K. Siems, S. M. Timofeev, P. Baumann, A. S. Ahmed, D. W. Müller, F. Mücklich, A. Haben, R. Kautenburger, R. Anton, C. Schaudinn, M. Laue, O. Schwengers, K. Runzheimer, K. Xanthopoulou, P. G. Higgins, S. Leuko, A. L. Boschert, Copper Stress Response of Antibiotic Resistant and Copper Tolerant <i>E. faecium</i> and efficacy of functionalized copper surfaces, <i>Adv. Mater. Interfaces</i> , 2025 , 12, e00430.
A. Haben, N. Bachmann, J.J. Langer, R. Kautenburger, Behaviour of Mo(VI), Eu(III) and U(VI) in Calcium-Silicate-Hydrate Phases: Immobilisation and Dynamic Remobilisation under Repository-Relevant Conditions, <i>Appl. Geochem.</i> , 2026 , 198, 106684.

E. Haettig, A. Haben, R. Kautenburger, M. Schneider, Delivery of siRNA and Chloroquine Through an Aspherical, Nanostructured Microparticle for Passive Targeting of Alveolar Macrophages and Inhibition of Local TNF- α Secretion, *Pharmaceutics*, **2026**, *18*, 154.

Not all of the publications listed in Table 1 were in direct connection to the topic of this doctoral thesis and will therefore not all be included in this work. In the course of the proposed doctoral project, the publication by Brix et al. [34] (2023, see Chapter 3.1.1), in which Aaron Haben was the second author, will be presented first. Furthermore, the publications by Haben et al. [12] (2024, see Chapter 3.1.2) and Haben et al. [8] (2026, see Chapter 3.1.3) will be included. Aaron Haben's exact contributions are described in detail in the respective chapters.

In addition to the peer-reviewed publications, further work has been conducted but has not yet been published in any scientific journals. This work focuses on the implementation/adaptation of a LA-ICP-QQQ methods for quantifying repository-relevant trace elements in cement alteration phases (more on this in Chapter 3.2.1).

To complete the scientific record, the two publications that were published before the start of the doctorate should also be listed – see Table 2.

Table 2: Peer-reviewed publications prior to the doctorate.

K. Brix, C. Hein, A. Haben, R. Kautenburger, Adsorption of caesium on raw Ca-bentonite in high saline solutions: Influence of concentration, mineral composition, other radionuclides and modelling, *Appl. Clay Sci.*, **2019**, *182*, 105275.

K. Brix, S. Baur, A. Haben, R. Kautenburger, Building the bridge between U(VI) and Ca-bentonite – Influence of concentration, ionic strength, pH, clay composition and competing ions, *Chemosphere*, **2021**, *285*, 131445.

3.1 Peer reviewed and published Results

3.1.1 Time-Dependent Retention of a Mixture of Cs(I), Sm(III), Eu(III) and U(VI) as Waste Cocktail by Calcium Silicate Hydrate (C-S-H) Phases

This research paper was submitted to “Minerals” on 18 October 2023 and published on 22 November 2023 (<https://doi.org/10.3390/min13121469>). The authors are Kristina Brix, Aaron Haben, and Ralf Kautenburger. The respective contributions of the authors to this work are listed in Table 3 in accordance with the CRediT (Contributor Roles Taxonomy) standard. The graphical abstract to this publication is shown in Figure 20.

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Table 3: Author contribution roles for the publication "Time-Dependent Retention of a Mixture of Cs(I), Sm(III), Eu(III) and U(VI) as Waste Cocktail by Calcium Silicate Hydrate (C-S-H) Phases" in form of the CRediT standard [34].

Contributor roles	Author(s)
Conceptualisation	Kristina Brix, Ralf Kautenburger
Methodology	Kristina Brix
Validation	Kristina Brix, Aaron Haben, Ralf Kautenburger
Formal analysis	Kristina Brix
Investigation	Kristina Brix, Aaron Haben
Writing – original draft preparation	Kristina Brix
Writing – review and editing	Kristina Brix, Aaron Haben, Ralf Kautenburger
Visualisation	Kristina Brix
Supervision	Ralf Kautenburger
Project administration	Ralf Kautenburger
Funding acquisition	Ralf Kautenburger

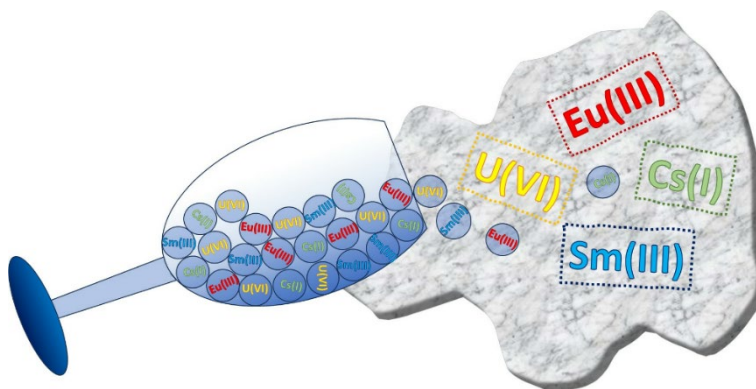


Figure 20: Graphical abstract to the publication "Time-Dependent Retention of a Mixture of Cs(I), Sm(III), Eu(III) and U(VI) as Waste Cocktail by Calcium Silicate Hydrate (C-S-H) Phases" [34].

Extended abstract:

The aim of this work was to investigate the time-dependent retention behaviour of a repository relevant waste cocktail (WC) of elements on the commercially available C-S-H phase Circosil®. This mainly consists of tobermorite with a C/S ratio of 0.83 and serves as a stable analogue to naturally aged C-S-H phases. The analysed WC contained the repository relevant elements Cs(I), Sm(III), Eu(III) and U(VI) as well as Zr(IV), Mo(VI), Ru(III) and Pd(II). However, this study only investigates the retention kinetics of the first four elements.

The kinetic batch experiments were conducted over a period of 217 d at alkaline pH > 10 and in highly saline electrolytes with an analyte concentration of $5 \cdot 10^{-7} \text{ mol L}^{-1}$. These background electrolytes were a diluted gypsum solution (DGS, $I = 2.6 \text{ M}$, pH = 10.6) as a reference for claystone pore water and a 0.1 M NaCl solution ($I = 0.1 \text{ M}$, pH = 10.9) as a simple comparison. To distinguish the influence of the adsorbent (Circosil®) from precipitation or adsorption on the centrifuge tube walls, experiments were carried out without the solid phase. For the quantification of the analytes ICP-MS and -QQQ were used.

The precipitation and wall adsorption results in the binary systems (without Circosil®) showed that Sm(III) and Eu(III) were almost quantitatively removed from the solution in both electrolytes (> 95%). This is mainly due to wall adsorption or precipitation on the tube walls. As expected, Cs(I) showed no relevant precipitation or wall adsorption, as it does not precipitate under natural conditions and the Na^+ ions (primary competitor to Cs^+) in the electrolyte saturate the tube wall. U(VI) forms negatively charged species at pH > 10, which makes adsorption on potentially negatively charged walls unlikely, which is reflected in the low retention values (4% – 13%).

In the ternary system, in the presence of Circosil®, the retention of all elements increased strongly, indicating the C-S-H phase as the preferred immobilisation mechanism. The retention of U(VI) in 0.1 M NaCl increased to > 97% and in DGS even to > 98%. In the case of Cs(I), a retention of only approx. 75% was observed at low ionic strength, which even fell to only approx. 14% in DGS. As Cs(I) and U(VI) showed little or no retention without Circosil®, surface precipitation can be ruled out, and the retention can be attributed to adsorption processes. In the case of Eu(III) and Sm(III), similar amounts as in the precipitation studies were retarded, but it could be shown that immobilisation on Circosil® is the

preferred mechanism. However, no difference between adsorption and surface precipitation could be identified in the experiments conducted.

The kinetic studies showed for Cs(I) that immobilisation probably takes place at strong binding sites of the C-S-H phases via inner-sphere complexes. In general, an equilibrium state was reached very quickly: in 0.1 M NaCl after 7 days (retention approx. 75%) and in DGS after only 3 d (retention approx. 14%). In the 0.1 M NaCl solution, adsorption even remained constant up to day 217, which indicates irreversible binding mechanism. Due to the high hydration energy of Cs(I), the inner-sphere adsorption sites are not accessible to most competing ions (such as Na⁺), but K⁺ (in the DGS) has access, and therefore explains the lower adsorption values therein. In relation to the competition of the other WC elements, the WC elements delayed the time to reach equilibrium compared to single element studies in the literature, suggesting competitive effects between the WC elements for adsorption sites. Overall, however, significant differences in R_d values to the ones from literature were observed, which is why it was concluded that the C/S ratio and the structure of the C-S-H phase (crystalline tobermorite in Circosil®) are more decisive for Cs(I) adsorption than the salt content or the initial concentration.

In the kinetic studies, the retention behaviour of Sm(III) and Eu(III) was identical. An equilibrium state was reached in the 0.1 M NaCl solution after 7 d and in the DGS after 28 d (in contrast to < 1 d in the literature). The difference to the literature is again explained by the competition of the WC elements for the sorption sites. For both analytes, 97% were retained in the 0.1 M NaCl solution. In addition to the significantly slower kinetics, slightly lower retention values were also observed in the DGS, which again confirms the influence of ionic strength and salt content.

In contrast to the other WC elements, no significant influence of the ionic strength on the retention kinetics of U(VI) on Circosil® was observed. In both cases, a state of equilibrium was reached after 7 d. A retention of approx. 99% was measured in the 0.1 M NaCl solution and approx. 95% in the DGS. These differences are not due to a competition effect, but due to increased Ca(II) leaching from the C-S-H phases at increased ionic strengths. With this fewer bridging Ca(II) ions are available for the adsorption of the uranyl anion, thus reducing retention. In comparison to single element studies from the literature, significantly slower kinetics were also observed here, which again suggests a competitive effect of the other WC elements at C-S-H binding sites.

In summary, the study proves that the commercial C-S-H phase Circosil® is a suitable substitute for wet-chemically synthesised phases for investigating the retention behaviour of Cs(I), Sm(III), Eu(III) and U(VI). Regarding this retention behaviour, a strong influence of the salt content of the background electrolytes was observed. With decreasing ionic strength, both the amount and the rate of retention increased for all four elements. A similar effect is observed with the competition of the WC elements. The studies in the WC show slower retention kinetics than comparable results in single-element studies. For Cs(I) and U(VI) in particular, immobilisation on Circosil® is the dominant mechanism, with the adsorption of Cs(I) via irreversible inner-sphere complexes to strong binding sites being the most likely. Furthermore, precipitation or incorporation into the C-S-H structure cannot be ruled out for Sm(III), Eu(III) and U(VI).



Article

Time-Dependent Retention of a Mixture of Cs(I), Sm(III), Eu(III) and U(VI) as Waste Cocktail by Calcium Silicate Hydrate (C-S-H) Phases

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Abstract: In the context of the safe storage of high-level radioactive waste, the time-dependent retention of a waste cocktail (WC) consisting of Zr(IV), Mo(VI), Ru(III), Pd(II), Cs(I), Sm(III), Eu(III) and U(VI) was studied on the commercially available C-S-H phase Circosil®. The herein presented results focus on Cs(I), Sm(III), Eu(III) and U(VI). Precipitation and wall adsorption studies in the absence of the solid phase show only a small amount of precipitation for Sm(III) and Eu(III) ($34 \pm 18\%$) in the high-saline diluted Gipshut solution (DGS, pH 10.6, $I = 2.6$ M). For Cs(I) and U(VI), no precipitation was observed. In 0.1 M NaCl (pH 10.9), the measured retention could completely be attributed to wall adsorption for all four elements. The obtained R_d values for the time-dependent retention of Sm(III), Eu(III) and U(VI) on Circosil® of 10^5 to 10^6 L·kg⁻¹ are in good agreement with the literature. For Cs(I) in the strongly saline background electrolytes, slightly higher R_d values of up to $8 \cdot 10^2$ L·kg⁻¹ were determined for the crystalline Circosil® compared to the wet chemical C-S-H phases. Overall, the commercial product Circosil® is suitable as an alternative to synthesised C-S-H phases to observe trends in the retention behaviour of these elements. Comparison between both background electrolytes shows an increase in the amount and velocity of retention for all four elements with decreasing salinity. This confirms adsorption processes as the fastest and initial retention mechanism. Precipitation or incorporation of Eu(III), Sm(III) and U(VI) cannot be ruled out in the long term. Comparing the kinetic of this WC study to single-element studies in the literature, a longer uptake time to reach a steady state of 7 d in 0.1 M NaCl and 28 d in DGS instead of <1 d was observed for Eu(III) and Sm(III). The situation for Cs(I) is similar. This indicates competing effects between the different WC elements for adsorption sites on the C-S-H phases.

Keywords: C-S-H phase; waste cocktail; high-level radioactive waste; caesium; europium; samarium; uranium; kinetic study; ICP-MS



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1. Introduction

Cement-based materials are going to be used in repositories for high-level radioactive waste (HLW) worldwide. They will be used as construction or sealing material for their physical and chemical stability and their ability to immobilise hazardous substances [1–3]. Calcium silicate hydrate (C-S-H) phases are the major hydration product of hardened cement and are mainly responsible for the retention of anions or cations [3]. C-S-H phases are mostly amorphous and degrade over time in contact with aqueous media. Due to leaching of Ca(II), the calcium to silicon ratio (C/S) decreases within approximately 36,000 years from 1.5 to 0.8 [4]. The resulting pore water has an alkaline pH between 12.5 and 10 decreasing with decreasing C/S ratio. The alteration of the C-S-H phases is very complex due to a lot of dissolution and precipitation processes taking place and the amorphousness of the material overall [3,5].

C-S-H phases used for retention experiments in the context of an HLW repository are mainly synthesised wet chemical or hydrothermal. Precursors are usually CaO and

SiO₂ which are mixed via a “direct reaction” method [1,6,7] with aqueous media like ultrapure water. Despite this simple preparation procedure, the pH values that naturally occur during equilibration with background electrolytes vary in the literature just like the retention for certain elements due to the complex processes involved in the formation and degradation [1,8,9]. At least, C-S-H phases are also sensitive to CO₂ [10–12]. CaCO₃ can be formed on the surface which lowers the adsorption potential.

The aim of this study is to investigate the time-dependent retention behaviour of a waste cocktail (WC) of elements relevant for HLW disposal on a stable, commercial C-S-H phase with defined structure: Circosil[®], which consists mainly (88%) of tobermorite with C/S = 0.83 and intercalated SiO₂ (10%) with traces (<0.5% each) of Al-, Mg-, Fe-, Ti-, K-, Na-, Zr-, Mn- and Cr-containing minerals [13]. At the end of the degradation process, C-S-H phases stabilise at a C/S ratio of ~0.8 and mostly have a structure similar to amorphous, disordered tobermorite [3,5,14–17]. Due to the complexity of the degradation process and possible heat release from the HLW, even crystallisation of the C-S-H phases cannot be ruled out [18,19]. All of this makes Circosil[®] a possible stable analogue to natural aged C-S-H phases. The WC consists of U(VI) representing the main component of the HLW inventory. The WC also contains Zr(IV), which is used as cladding for fuel rods in nuclear reactors [20,21], and Sm(III) which can be used as a neutron adsorber in control rods [22,23]. Additionally, the possible fission products Mo(VI), Ru(III), Pd(II), Cs(I) and Eu(III) are contained in the WC whereas Eu(III) and Sm(III) also act as homologues to Am(III) and Cm(III) [24–26].

In this study, the focus lies on experiments at pH values > 10. These pH values are naturally obtained during the equilibration of C-S-H phases with aqueous media. The used background electrolytes are highly saline (I = 0.1 M and 2.6 M) because host rocks for potential HLW disposals may be salt formations or in contact with salt dome deposits which results in highly saline pore waters [27–29]. Retention studies with such ionic strengths are scarce [14,30–35]. We used diluted Gipshut solution (DGS, I = 2.6 M) which is a reference pore water of claystone in northern Germany and 0.1 M NaCl as a simple and lower-saline comparative medium.

Finally, we present the retention results of Cs(I), Sm(III), Eu(III) and U(VI) as part of the WC on Circosil[®] over 217 d and elucidate the retention mechanisms in the nanomolar concentration range. Since the HLW must be stored safely for hundreds of thousands of years, knowledge of the immobilisation mechanisms is mandatory. So far, several attempts have already been made in the literature to clarify the retention and binding mechanism of these elements on cementitious materials ([3] and references within). The results vary depending on the initial concentrations and used analytical method. For most of these WC elements, it is difficult to elucidate the mechanism in detail because precipitation could occur even in the nanomolar concentration range. Additionally, many analytical methods are not sensitive enough to detect analyte concentrations in the picomolar range, which remain in the liquid phase for many elements that adsorb strongly to the solid phases, such as Sm(III) or Eu(III). The amorphous and changing structure with C/S ratio of the C-S-H phases make solids analysis even worse. The possible retention mechanisms observed so far for the four elements of interest are shortly summarised in the following.

For Cs(I), mainly ion exchange processes come into charge as the binding mechanism because it does not precipitate under natural conditions. Incorporation was also observed by Iwaida et al. [36] at a very high Cs(I) concentration. As already mentioned, observations in the literature for the uptake of radionuclides on C-S-H phases may vary a lot. A clear dependence of the Cs(I) adsorption on the initial concentration was observed by Missana et al. [37]. This is a strong indicator for different binding sites. Meanwhile, Atkinson and Nickerson [38] found the sorption isotherm to be linear. Therefore, one to three different adsorption sites (ion exchange, outer-sphere and inner-sphere complexes) are suggested in the literature for Cs(I) adsorption on cementitious materials [39–43].

For Eu(III), and Sm(III) as chemically very similar rare earth elements (and as homologues to Am(III) and Cm(III)), three retention mechanisms on cementitious materials

or C-S-H phases are proposed in the literature: adsorption, incorporation and precipitation [14,26,44–48]. Each of these studies observed high up to quantitative retention for both elements. This is either explained by the high affinity of the three valent cations to the negatively charged surface of the adsorbent material or precipitation due the alkaline background electrolyte.

Adsorption on the negatively charged surface of C-S-H phases seems unlikely for U(VI) at $\text{pH} > 10$ because it forms negatively charged carbonate or hydroxy complexes [30,49–51]. Nevertheless, high retention of U(VI) on cementitious materials is observed in many studies. It occurs through precipitation [2,9], incorporation [52], direct surface complexation [2,49,51,53,54] or ternary surface complexes involving Ca(II) [30,55,56]. Tits et al. [57] even observed three U(VI) species in their study which they attributed to surface complexation, an incorporated species and a uranate-like precipitate.

Altogether, the precipitation and wall adsorption experiments performed in this study, as well as different saline background electrolytes, WC elements as competing ions and the dynamic behaviour during the kinetic study, provide new insights into the retention mechanisms of Cs(I), Sm(III), Eu(III) and U(VI) on C-S-H phases.

2. Materials and Methods

2.1. Chemicals and Standards

All solutions were prepared with ultrapure water ($0.055 \mu\text{S}\cdot\text{cm}^{-2}$) from a PURELAB® Chorus 1 ultrapure water filtration unit (Elga LabWater, High Wycombe, UK). For the preparation of the background electrolytes, NaCl, CaCl_2 , Na_2SO_4 and KCl salts of premium-grade quality (EMSURE®) from the company Merck (Darmstadt, Germany) were used. Sc ($1 \text{ g}\cdot\text{L}^{-1}$, Alfa®, Karlsruhe, Germany) and Ho ($1 \text{ g}\cdot\text{L}^{-1}$, Merck Certipur®, Darmstadt, Germany) served as internal standards and HNO_3 (ROTIPURAN® Supra 69%, Carl Roth, Karlsruhe, Germany) for acidifying the measurement solutions for mass spectrometry with inductively coupled plasma (ICP-MS). To prepare the samples and the calibrations for the measurements, the following elemental standards were used: Si(IV) ($10 \text{ g}\cdot\text{L}^{-1}$, AccuStandard, New Haven, CT, USA), Ca(II) ($1 \text{ g}\cdot\text{L}^{-1}$, Merck Certipur®, Darmstadt, Germany), Zr(IV) ($10 \text{ g}\cdot\text{L}^{-1}$, Merck Supelco®, Darmstadt, Germany), Mo(VI) ($1 \text{ g}\cdot\text{L}^{-1}$, Fluka, Buchs, Switzerland), Ru(III) ($1 \text{ g}\cdot\text{L}^{-1}$, Merck, Darmstadt, Germany), Pd(II) ($1 \text{ g}\cdot\text{L}^{-1}$, Fluka, Buchs, Switzerland), Cs(I) ($1 \text{ g}\cdot\text{L}^{-1}$, AccuStandard, New Haven, CT, USA), Sm(III) ($1 \text{ g}\cdot\text{L}^{-1}$, Alfa Aesar Specpure®, Karlsruhe, Germany), Eu(III) ($10 \text{ g}\cdot\text{L}^{-1}$, Agilent, Kingstown, MD, USA) and U(VI) ($1 \text{ g}\cdot\text{L}^{-1}$, AccuStandard, New Haven, CT, USA). The C-S-H phases used are commercially available Circosil® 0.1 from Cirkel (Emsdetten, Germany). NaOH (Suprapur® 30%, Merck, Darmstadt, Germany) and HCl (HCl 30% Suprapur®, Merck Supelco®, Darmstadt, Germany) were used to adjust the desired pH of the precipitation and wall adsorption experiments.

2.2. Experiments and ICP-MS Samples

For the batch experiments, the two electrolytes 0.1 M NaCl and DGS (2.5 M NaCl, 0.02 M $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$, 0.008 M Na_2SO_4 and 0.005 M KCl) were prepared.

For the kinetic experiments, 800 mg Circosil® were weighed in 250 mL LDPE bottles and 200 mL of the respective electrolyte was added ($\text{S/L} = 4 \text{ g}\cdot\text{L}^{-1}$). After 7 d equilibration in a horizontal shaker (Promax 1020 platform shaker, Heidolph Instruments, Schwabach, Germany), the pH was measured. It settled naturally to 10.9 in 0.1 M NaCl and 10.6 in DGS. According to Altmaier et al. [58], a pH correction of +0.5 was made in the high-saline DGS. Afterwards, the analytes (Zr(IV), Mo(VI), Ru(III), Pd(II), Cs(I), Sm(III), Eu(III) and U(VI)) were added at a concentration of $500 \text{ nmol}\cdot\text{L}^{-1}$. Changes in the pH values due to the addition of acidic element standards were corrected with NaOH and adjusted to the former value of 10.9 or 10.6, respectively. Sampling of 1 mL each was performed after 1 h, 1 d, 3 d, 7 d, 14 d, 28 d, 56 d, 112 d, 168 d and 217 d. Each experiment was prepared in independent triplicates. Reference experiments without analyte were performed for background and leaching correction.

For the wall adsorption studies, polypropylene (PP) centrifuge tubes (Ultra-High Performance Centrifuge Tube, VWR International, Darmstadt, Germany) were filled with either 10 mL 0.1 M NaCl or DGS. After that, Zr(IV), Mo(VI), Ru(III), Pd(II), Cs(I), Sm(III), Eu(III) and U(VI) were added at the concentration of $500 \text{ nmol} \cdot \text{L}^{-1}$. To mimic the amounts of Si(IV) and Ca(II) leached by Circosil[®], $1 \text{ mg} \cdot \text{L}^{-1}$ each was added and additionally the pH was adjusted analogous to the kinetic study (0.1 M NaCl: 10.9; DGS: 10.6). After 7 days, 1 mL of sample was taken from each, and the lowest part of the PP tube, holding 1 mL, was removed and discarded. The upper part of the tube was soaked in 5% HNO₃ for at least one hour. Afterwards, this solution was also sampled.

2.3. The ICP-MS System

To quantify the samples with 0.1 M NaCl as background electrolyte, the WC elements were analysed by ICP-MS (Agilent 8900 ICP-QQQ, Santa Clara, CA, USA) using an Agilent SPS4 autosampler and a high matrix introduction system for higher salt concentrations up to 3% (HMI, Agilent) via a standard method.

The ionic strength of the DGS is higher than the commercial system can handle. Therefore, a transient ICP-MS method according to Hein et al. [59] was used. For this purpose, a 7500cx ICP-MS (Agilent, Santa Clara, CA, USA) was used with a CETAC autosampler (ASX 500) and an HMI system (Agilent). This method allows quantification of elements in up to 5 M saline solutions without further dilution or sample cleanup steps. Therefore, a supplemental solution is used to ensure a constant flow to the nebuliser (which also results in an on-line sample dilution of about 1:4), the sample acquisition time is shortened to 10 s and time-resolved measurements are performed.

All ICP-MS measurement solutions were prepared to a total volume of 10 mL and the solutions contained 5% HNO₃ and $10 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ each of Sc and Ho as internal standards. The quantification for both methods was performed by external calibration with concentrations from 0.001 to $20 \text{ } \mu\text{g} \cdot \text{L}^{-1}$.

3. Results

3.1. Precipitation and Wall Adsorption

Concerning the retention of heavy metals, many different processes can play a role. To differentiate between the influence of the adsorbent material and precipitation due to oversaturation or wall adsorption on the PP tubes in the alkaline pH range, batch experiments in the binary system (background electrolyte and analytes) and in the ternary system (C-S-H phase, background electrolyte and analytes) were conducted.

For all investigated elements, precipitation and wall adsorption were investigated as competing processes to the immobilisation on the C-S-H phase. Sm(III) and Eu(III) tend to precipitate at high pH values as hydroxides or carbonates [60–62] whereas the critical phases for U(VI) are Na₂U₂O₇ and CaUO₄ [3,63]. Cs(I) does not precipitate under natural conditions.

The results in the binary system (without adsorbent material) can be seen in Figure 1. Sm(III) and Eu(III) are almost quantitatively removed out of both background electrolytes ($\geq 95\%$). Additionally, wall adsorption or precipitation on the tube wall plays a major role in DGS with $93 \pm 4\%$ (Eu(III)) and $92 \pm 4\%$ (Sm(III)) in 0.1 M NaCl and $65 \pm 19\%$ (Eu(III)) and $64 \pm 18\%$ (Sm(III)). The smaller amount in DGS can be explained by wall saturation with ions from the background electrolyte.

For U(VI), only a low retention of $13 \pm 2\%$ in 0.1 M NaCl and $4 \pm 4\%$ in DGS can be observed. In DGS, the retention can be completely described by wall adsorption or wall precipitation. In 0.1 M NaCl, the share of wall adsorption is only $8 \pm 1\%$. This agrees with the findings of Baqer et al. [54] that the nucleation kinetic of U(VI) is too slow to take place in most ordinary laboratory experiments.

The clear differences between Eu(III), Sm(III) and U(VI) in the precipitation/wall adsorption behaviour can be explained by the speciation in solution. U(VI) forms the two-fold-charged uranyl cation determining complexation and speciation behaviour whereas

for Eu(III) and Sm(III) the three-fold-charged cations are defining. At pH 10.5–11, U(VI) forms negatively charged species in solution (mainly $\text{UO}_2(\text{OH})_3^-$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$) which tend not to adsorb on the potential negatively charged tube wall [30]. The main species for Eu(III) are $\text{Eu}(\text{OH})_3$ and $\text{Eu}(\text{CO}_3)_2^-$ [64] which have a higher affinity for wall adsorption under these conditions.

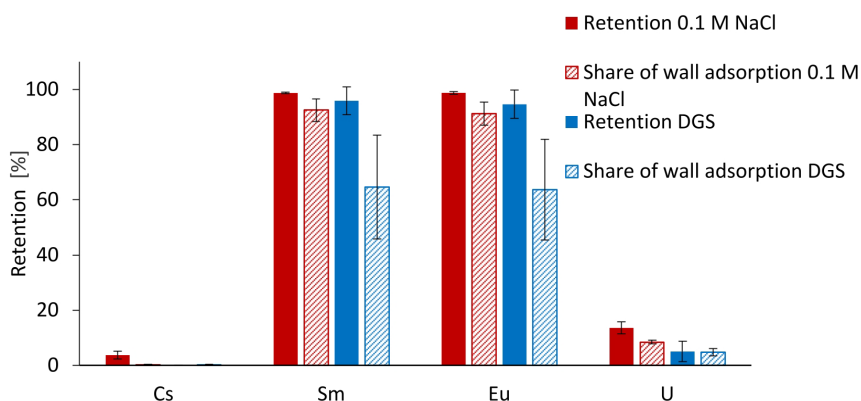


Figure 1. Retention of Cs(I), Sm(III), Eu(III) and U(VI) (initial concentration: $1 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$) after 7 d in 0.1 M NaCl (red, pH 10.9) and diluted Gipshut solution (DGS, blue, pH 10.6) and the share of wall adsorption (hatched) in the binary system (background electrolyte and analytes), also in the presence of $1 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Zr(IV), Mo(VI), Ru(III) and Pd(II), respectively, and $1 \text{ mg} \cdot \text{L}^{-1}$ Si(IV) and Ca(II).

As expected, no relevant precipitation or wall adsorption can be detected for the single-charged Cs(I). Even in the lower saline 0.1 M NaCl solution, the excess of Na(I) is 200,000-fold more than that of Cs(I). It can be assumed that this excess saturates the tube wall.

In the presence of Circosil® (Figure 2), the retention of Cs(I) and U(VI) increases strongly: in 0.1 M NaCl from $3 \pm 1\%$ to $59 \pm 1\%$ for Cs(I) and from $13 \pm 2\%$ to $97 \pm 1\%$ for U(VI), respectively. In DGS, the immobilisation increased for Cs(I) from 0% to $14 \pm 3\%$ and for U(VI) from $4 \pm 4\%$ to $98.7 \pm 0.3\%$.

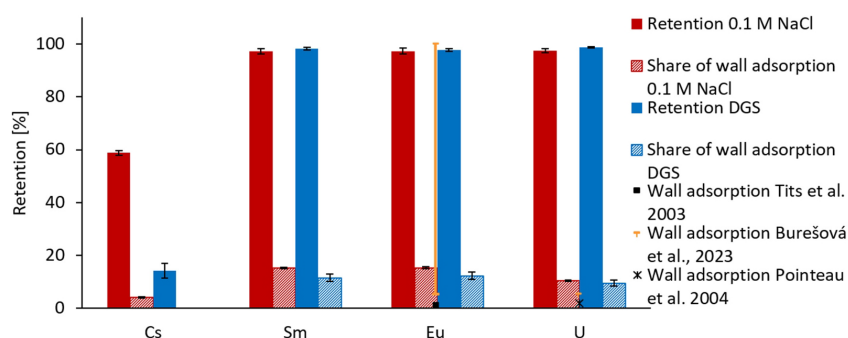


Figure 2. Retention of initial $1 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Cs(I), Sm(III), Eu(III) and U(VI) on Circosil® (7 d equilibrium time) in 0.1 M NaCl (red, pH 10.9) and diluted Gipshut solution (DGS, blue, pH 10.6) and the share of wall adsorption (hatched), also in the presence of Zr(IV), Mo(VI), Ru(III) and Pd(II). Data points refer to wall adsorption from previous studies: $<1\%$ and 6.5% – 100% for Eu(III) [26,44] and $<2\%$ and $<5\%$ for U(VI) [44,51].

The amount of wall adsorption involved in the retention decreases to $\leq 15\%$ for each element studied. Especially for Eu(III) and Sm(III), it can be clearly seen that the immobilisation on Circosil® is the preferred retention mechanism compared to wall adsorption

and classic precipitation in the binary system without adsorbent material. In the literature, wall adsorption of Eu(III) [26,44] and U(VI) [44,51] on PP tubes in the presence of C-S-H phases and hydrated cement paste was also investigated. While Tits et al. [26] observed wall adsorption <1% for Eu(III), the results gained by Burešová et al. [44] and Pointeau et al. [51] are similar to this study. They found only a small amount of U(VI) adsorbed on the wall (<2 or <5%, $c(\text{U(VI)}) = 4 \cdot 10^{-9} - 7 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$). For Eu(III), the adsorbed amount was 6.5%–100% depending on the solid-to-liquid ratio and the present adsorbent material. Burešová et al. [44] explained it by the adsorption of cement or C-S-H colloids on the wall where Eu(III) or U(VI) is immobilised. The same observation was made in this study as even after centrifugation, small particles were visible in the upper part of the liquid phase and on the tube wall. These particles could either be C-S-H phase or leached SiO_2 . So, the observed wall adsorption can be retention on the C-S-H phase which adhered on the wall until desorption with HNO_3 .

These experiments show a clear involvement of Circosil® in the retention of all four elements. U(VI) and Cs(I) show almost no retention in the absence of the C-S-H phase, so surface precipitation may be excluded, and the retention should be driven by adsorption processes. Nevertheless, it is not possible to distinguish between adsorption or surface precipitation processes for Eu(III) and Sm(III). The wall adsorption observed for both elements in the absence of Circosil® could be attributed to wall precipitation of nanoscale solids due to the larger surface area on the wall of the PP tubes (approximately 36 cm^2) compared to the tube's bottom (approximately 2 cm^2). The surface of Circosil® is $65 \text{ m}^2 \cdot \text{g}^{-1}$ [15] which equals 2.6 m^2 for the 40 mg used in the experiment. This exceeds the tube's surface by far and means the C-S-H phase is the preferred place for possible precipitation and adsorption.

3.2. Time-Dependent Retention of Cs(I)

A steady state is settled very fast by the time-dependent adsorption of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Cs(I) on Circosil® (Figure 3). After 7 d in 0.1 M NaCl and 3 d in DGS, an adsorption of $75 \pm 1\%$ or $14 \pm 1\%$ is reached, respectively. It does not change until 217 d in 0.1 M NaCl which shows an irreversible binding of Cs(I) on the C-S-H phase in this stationary experiment. In DGS, a slight decrease from 15% after 112 d to 9% after 217 d is visible. The three independent experimental rows show only slight variations of <3%. The influence of the background electrolyte's salinity on the Cs(I) adsorption can clearly be seen as the adsorption decreases strongly with the increased Na(I) concentration from 0.1 M NaCl to 2.5 M NaCl in DGS. This agrees with the literature [3,31,65]. Nevertheless, it is remarkable that adsorption of Cs(I) still takes place despite a 5-million-fold excess of Na(I) in DGS.

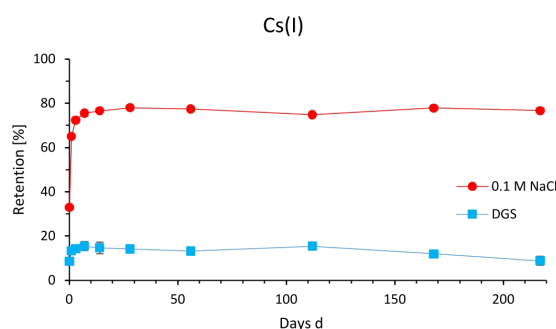


Figure 3. Time-dependent adsorption of initial $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Cs(I) on Circosil® in 0.1 M NaCl (red dots, pH 10.9) and diluted Gipshut solution (DGS, blue squares, pH 10.6), also in the presence of Sm(III), Eu(III), U(VI), Zr(IV), Mo(VI), Ru(III) and Pd(II). Lines between the measurement points are only drawn for clarification.

These observations are in contrast with a recent kinetic study on a synthesised C-S-H phase ($C/S = 1.08$). There, in 0.1 M NaCl, Cs(I) adsorption was only remarkably detectable after 28 d ($7 \pm 0\%$) for the initial $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Cs(I) and increased until the end of the experiment (112 d, $15 \pm 2\%$) [14]. Not only was the kinetic much slower, the total amount of immobilised Cs(I) is also around five times lower than on the commercial C-S-H phase. In DGS, Cs(I) adsorbed on the synthesised C-S-H phase after 1 h and 1 d, but afterwards, no adsorption could be detected anymore [14]. This is also in contrast with the current study. A reason for this may be the differences in the C/S ratio. The capability of Cs(I) immobilisation increases with decreasing C/S ratio due to the decreasing amount of Ca(II) blocking potential binding sites [37,65–68]. With respect to the high Na(I) concentration, the $2 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ Ca(II) in DGS and the other competing WC elements, the lower C/S ratio of Circosil® (0.83) cannot be the only explanation for this phenomenon. It also does not fit modelled data where an increase in the C/S ratio from 0.83 to 1.25 led to a decrease in Cs(I) adsorption from 37% to 23% in the micromolar concentration range [65]. The other difference between the C-S-H phases is the crystallinity and, consequently, the kind and amount of possible binding sites for Cs(I). Wet chemical synthesised C-S-H phases are amorphous and poorly crystalline [69] whereas the structure of the hydrothermal manufactured commercial product equals an 11-Å tobermorite [13]. This could enhance the Cs(I) adsorption capacities [69,70].

Three adsorption sites are considered in theoretical models for the Cs(I) uptake on C-S-H phases: ion exchange and surface complexation on weak or strong binding sites [37,39,43]. The latter have only a low capacity compared to the other sites. According to Duque-Redondo et al. [39], the weak sites represent outer-sphere and the strong sites inner-sphere surface complexes. In this study, it is very likely that the adsorbed Cs(I) is immobilised mainly on the strong binding sites via inner-sphere complexes. Because of the high hydration energy, these sites are considered non-accessible for most competing ions such as Na(I) or the elements present in the WC. Only K(I) from the DGS has access to these sites which contributes to the lowered adsorption in DGS compared to 0.1 M NaCl [41,71–73]. Also in molecular dynamics simulations, Cs(I) tends to adsorb as inner-sphere complexes on tobermorite [74]. Another hint for the Cs(I) adsorption on the strong sites is the immobilisation's irreversibility. Iwaida et al. [30] observed an incorporation in the C-S-H structure at high Cs(I) concentrations ($1 \text{ mol} \cdot \text{L}^{-1}$) which is also irreversible. Incorporation processes take place on a long timescale. So, it is not very likely to be the initial retention mechanism in this study where a steady state is reached after three to seven days. Nevertheless, a small decrease in Cs(I) adsorption in DGS is visible over time. It is possible that K(I) displace Cs(I) from the strong binding sites on a long timescale.

In the kinetic study of Missana et al. [37], a steady state of the Cs(I) adsorption on a C-S-H gel ($C/S = 0.8$) was already reached at the first measurement point after 1 d in deionised water. Also, Arayro et al. [66] calculated fast steady state settling of 1 d for Cs(I) on a modified 11-Å tobermorite. This contrasts with our results where the Cs(I) adsorption stays constant after 7 d (0.1 M NaCl) or 3 d (DGS). The difference can be explained either by the competing ions of the background electrolytes or by the elements of the WC competing for fast accessible binding sites such as ion exchange sites. This agrees with the results of Li and Pang [75]. They observed a characteristic adsorption time for Cs(I) on mortar in a high-saline pore solution ($I = 0.23 \text{ M}$) of 0.44–0.6 d, but a quasi-steady state was only reached after 7 d. Furthermore, they also investigated the influence of Sr(II) on the time-dependent Cs(I) adsorption and found a small decrease in the adsorbed Cs(I) amount. As their background electrolyte already contained $40 \text{ mg} \cdot \text{L}^{-1}$ of Ca(II), the additional impact of $2.8 \cdot 10^{-10} \text{ mol} \cdot \text{L}^{-1}$ Sr(II) is remarkable. This highlights the importance of retention studies in the presence of possible competing ions not only from the background electrolyte but also from the radioactive inventory. Nevertheless, the investigated concentration of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ of the WC elements may be too low to see a competing effect with Cs(I) compared to the concentrations of the background electrolyte's components because for

the Cs(I) adsorption on bentonite in similar media, an effect was only visible at an analyte concentration of $2.5 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ [31].

At least, the steady state of the Cs(I) adsorption on Circosil® is reached earlier in the higher-saline solution (DGS, 3 d) than in 0.1 M NaCl (7 d). This behaviour could be explained by the amount of adsorbed Cs(I). In 0.1 M NaCl, around 5 times more Cs(I) ($75 \pm 1\%$, $3.7 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$) is bound to Circosil® than in DGS ($14 \pm 1\%$, $7 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$). The strong binding sites with low capacity are not easily accessible, so the larger amount of Cs(I) which is able to get there in 0.1 M NaCl needs more time.

In Table 1, the distribution coefficients R_d [$\text{L} \cdot \text{kg}^{-1}$] for Cs(I) are shown at different times in 0.1 M NaCl and DGS. The coefficient is normally written as K_d , representing the ratio of the element's amount bound to the solid and the amount in the liquid phase. Since precipitation of Sm(III), Eu(III) and U(VI) may not be completely excluded, all values are represented by R_d for consistency. The R_d values for Cs(I) in the literature are broadly scattered and depend mainly on the salinity of the background electrolytes, on the C/S ratio and the initial Cs(I) concentration but also on the adsorbent material's structure [3]. In this study, they range between 100 and $900 \text{ L} \cdot \text{kg}^{-1}$ in 0.1 M NaCl with an average of $830 \pm 60 \text{ L} \cdot \text{kg}^{-1}$ in the steady state after 7 d. The gained values are at the upper end of or even higher than the range reported in the literature despite the comparatively higher ionic strength [37,65]. As expected, the R_d values in DGS are with $23\text{--}46 \text{ L} \cdot \text{kg}^{-1}$ lower due to the high salinity and presence of a K(I) excess. The average value is $39 \pm 7 \text{ L} \cdot \text{kg}^{-1}$. Values in the same range were also found by Missana et al. [37] for C/S = 1.0 after equilibration in deionised water. Baur et al. [14] also observed lower R_d values in identical background electrolytes but with a higher C/S ratio (1.08). This leads to the conclusion that the C/S ratio and the structure of the C-S-H phase are more critical parameters for the Cs(I) adsorption than salinity or the initial concentration.

3.3. Time-Dependent Retention of Sm(III) and Eu(III)

The time-dependent retention of Eu(III) and Sm(III) on the commercial C-S-H phase Circosil® is shown in Figure 4. As both elements are trivalent actinides and the physical and chemical properties rarely differ, the retention behaviour is extremely similar. After 7 d of equilibration time, $97 \pm 1\%$ of the analytes are removed from the liquid phase in 0.1 M NaCl. The retention stays constant over the observed period with only one exception after 112 d where it decreases to $86 \pm 4\%$. The kinetic is slower and the overall retention of Sm(III) and Eu(III) is lower in DGS. Additionally, 7 d were needed to reach an immobilisation of $88 \pm 2\%$ which slowly increases further to $99.7 \pm 0.6\%$ after 168 d. Afterwards, the retention decreases to $87 \pm 6\%$ again.

Table 1. Distribution coefficients R_d for the retention of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Cs(I) on Circosil® in 0.1 M NaCl (pH 10.9) and diluted Gipshut solution (DGS, pH 10.6) at ten different sampling times (also in the presence of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Sm(III), Eu(III), U(VI), Zr(IV), Ru(III), Mo(VI) and Pd(II)).

Equilibration Time [d]	$R_d(\text{Cs(I)})$ in 0.1 M NaCl [$10^3 \text{ L} \cdot \text{kg}^{-1}$]	$R_d(\text{Cs(I)})$ in DGS [$10^3 \text{ L} \cdot \text{kg}^{-1}$]
0.04	0.123 ± 0.004	0.023 ± 0.004
1	0.46 ± 0.02	0.038 ± 0.002
3	0.65 ± 0.05	0.041 ± 0.004
7	0.77 ± 0.04	0.046 ± 0.007
14	0.82 ± 0.02	0.043 ± 0.009
28	0.89 ± 0.03	0.041 ± 0.006
56	0.86 ± 0.05	0.038 ± 0.006
112	0.74 ± 0.03	0.046 ± 0.006
168	0.88 ± 0.03	0.034 ± 0.004
217	0.82 ± 0.04	0.024 ± 0.006

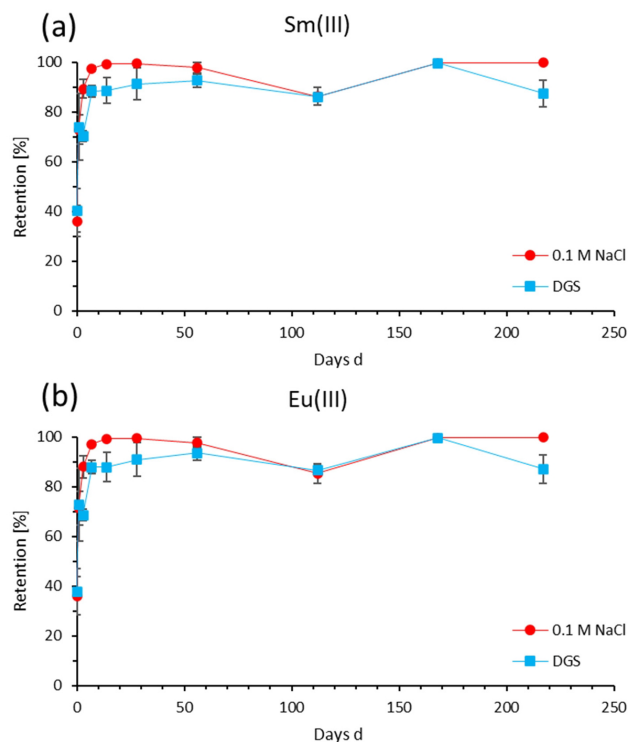


Figure 4. Time-dependent retention of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Sm(III) (a) and Eu(III) (b) on Circosil® in 0.1 M NaCl (red dots, pH 10.9) and diluted Gipshut solution (DGS, blue squares, pH 10.6), also in the presence of Cs(I), U(VI), Zr(IV), Mo(VI), Ru(III) and Pd(II). Lines between the measurement points are only drawn for clarification.

A small drop in the immobilised amount of Sm(III) and Eu(III) can also be seen after 112 d ($86 \pm 2\%$) for both background solutions. The reproducibility of the measured data is worse in DGS with a standard deviation of $>5\%$ at five measurements points (15% after 1 d at maximum) than in 0.1 M NaCl (two measurement points $>5\%$, 8% after 1 h at maximum). Despite the similar behaviour, the immobilisation of Sm(III) on Circosil® is slightly preferred over Eu(III). With only one exception (after 112 d in DGS), the retention of Sm(III) is up to 2 percentage points (pp) higher and the standard deviations lower at every measurement point than for Eu(III).

In the literature, three retention mechanisms are proposed for Eu(III): precipitation, incorporation and surface complexation [26,45,47,48]. The negative influence of increasing ionic strength on the retention behaviour in this study indicates retention mechanisms where competing effects play a role. This let incorporation or surface complexation appear to be the preferred mechanisms which was also observed by Mandaliev et al. [46]. Tits et al. [26] proposed precipitation followed by incorporation to be responsible for the retention of Cm(III) at pH 13.3. In this case, we would expect a positive influence of the salinity in our experiment. Nevertheless, the dynamic behaviour of Eu(III) and Sm(III) in this study after 56 d can be a hint for several retention processes taking place. Parts of the adsorbed lanthanides can slowly become incorporated in the C-S-H phase's structure. Precipitation, e.g., as $\text{Ln}(\text{OH})_3$ or $\text{Ln}_2(\text{CO}_3)_3$ (Ln = lanthanide), cannot completely be ruled out on the longer timescale. The $>70\%$ immobilisation after 1 d for both elements hints to a fast process influenced by competing ions. Surface complexation fits this very well. The

slightly lower affinity for Eu(III) may be caused by competing effects between Eu(III) and Sm(III) or due to different ionic properties.

A comparison between this study and a kinetic study on a synthesised C-S-H phase ($C/S = 1.08$) shows similarities in the retention behaviour of Eu(III) [14]. It is immobilised fast and almost quantitatively. The retention stays dynamic over the observed timescale of 112 d. Despite this, the retention process for $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Eu(III) is faster in DGS than in 0.1 M NaCl which is in contrast to the study presented here. The authors explained the Eu(III) retention mainly by precipitation, but no wall adsorption was investigated in their precipitation experiments. Their study was carried out at higher pH values (pH 12.5–13) than the present study. Eu(III) undergoes a change in speciation between pH 10.5 and 13 [64]. This can enhance the precipitation of Eu(III), e.g., as $\text{Eu}(\text{OH})_3$. A retention >90% is reached after 1 d in 0.1 M NaCl and DGS [14] which contrasts with the current study where equilibration times of 7 d and 28 d were needed, respectively. In other studies, Eu(III) or Sm(III) retention of >90% on cementitious materials is reached within several minutes to 1 d [26,44,47,48,76]. Reasons for this may be the competition for binding sites between Eu(III), Sm(III) and other elements present in this study or higher analyte concentrations or pH values in the literature which favour precipitation.

In the kinetic study of Tits et al. [26] on C-S-H phases ($C/S = 1$) in a mixture of NaOH and KOH ($I \sim 0.3 \text{ M}$), without trivalent competing ions, Eu(III) retention was also constant after 1 d of equilibration time. The R_d values were $60 \pm 30 \cdot 10^3 \text{ L} \cdot \text{kg}^{-1}$ in the same order of magnitude as in the present study in 0.1 M NaCl after 14 d (Table 2). The R_d values in high-saline DGS are one order of magnitude lower. The high uncertainties, especially at high R_d values, result from the very low concentrations (c_{eq}) measured in the supernatant. After 217 d, the three measured concentrations in the 0.1 M NaCl supernatant for Sm(III) were $0.17 \cdot 10^{-9}$, $1.7 \cdot 10^{-9}$ and $1.9 \cdot 10^{-9} \text{ mol} \cdot \text{L}^{-1}$. In absolute numbers, the resulting R_d values are $730 \cdot 10^3$, $72 \cdot 10^3$ and $67 \cdot 10^3 \text{ L} \cdot \text{kg}^{-1}$. This results in a deviation for R_d larger than the average value.

Table 2. Distribution coefficients R_d for the retention of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Sm(III) and Eu(III) on Circosil® in 0.1 M NaCl (pH 10.9) and diluted Gipshut solution (DGS, pH 10.6) at ten different sampling times (also in the presence of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ Cs(I), U(VI), Zr(IV), Ru(III), Mo(VI) and Pd(II)).

Equilibration Time [d]	$R_d(\text{Sm(III)})$ in 0.1 M NaCl [$10^3 \text{ L} \cdot \text{kg}^{-1}$]	$R_d(\text{Eu(III)})$ in 0.1 M NaCl [$10^3 \text{ L} \cdot \text{kg}^{-1}$]	$R_d(\text{Sm(III)})$ in DGS [$10^3 \text{ L} \cdot \text{kg}^{-1}$]	$R_d(\text{Eu(III)})$ in DGS [$10^3 \text{ L} \cdot \text{kg}^{-1}$]
0.04	0.14 ± 0.04	0.14 ± 0.05	0.18 ± 0.07	0.16 ± 0.06
1	0.7 ± 0.2	0.6 ± 0.2	0.9 ± 0.6	0.9 ± 0.6
3	2 ± 0.7	1.8 ± 0.7	0.60 ± 0.06	0.55 ± 0.06
7	9 ± 4	8.5 ± 3.4	1.9 ± 0.4	1.8 ± 0.4
14	37 ± 9	35 ± 8	2.3 ± 1.2	2.2 ± 1.1
28	41 ± 16	38 ± 13	4 ± 3	4 ± 3
56	11 ± 12	11 ± 11	3.4 ± 1.3	4 ± 2
112	1.6 ± 0.4	1.4 ± 0.4	1.6 ± 0.2	1.6 ± 0.3
168	79 ± 60	82 ± 66	>100 *	>50 *
217	290 ± 380	770 ± 1200	2 ± 1	2 ± 1

* At least one of the triplicates was below the detection limit.

Similar to the study of Baur et al. [14], the study by Tits et al. [26] was carried out at a significantly higher pH value (13.3) and the authors suggest precipitation as the first occurring retention mechanism. Häußler et al. [77] investigated the retention of $1 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ Am(III) on C-S-H phases with different C/S ratios and consequently different pH values in the range of 10.2–12.6. After 72 h of equilibration time, no relevant differences in the adsorption behaviour were noticeable with >98% retention for all experiments. The R_d values are $3 \cdot 10^4$ to $1 \cdot 10^6 \text{ L} \cdot \text{kg}^{-1}$, in agreement with the literature and in the range of this study. Häußler et al. [77] explained the retention with surface complexation on silanol groups as the chosen actinide concentrations are under the solubility limit. The

kinetic in the study of Häußler et al. [77] is faster than in the current study, independent of the pH value and with most likely surface complexation as the preferred retention mechanism. Similar observations were made by Pointeau et al. [47] where the amount of unadsorbed Eu(III) was under the limit of detection for every C/S ratio they investigated. This indicates a strong influence of the competing ions (WC and background electrolyte) on the retention kinetic of Eu(III) and Sm(III), which were not present in study of Häußler et al. [77] or Pointeau et al. [47].

3.4. Time-Dependent Retention of U(VI)

In Figure 5, the time-dependent retention of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ U(VI) on Circosil® in 0.1 M NaCl and DGS can be seen. U(VI) has a faster retention kinetic than the other investigated WC elements.

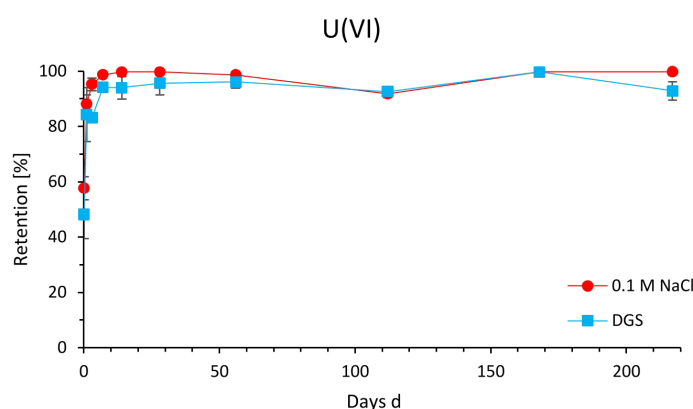


Figure 5. Time-dependent retention of $5 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ U(VI) on Circosil® in 0.1 M NaCl (red dots, pH 10.9) and diluted Gipshut solution (DGS, blue squares, pH 10.6), also in the presence of Cs(I), Sm(III), Eu(III), Zr(IV), Mo(VI), Ru(III) and Pd(II). Lines between the measurement points are only drawn for clarification.

In 0.1 M NaCl, the retention increased to >95% after 3 d and after 7 d a steady state of around 99% retention is reached. The retention in DGS is noticeably lower (mainly for the first 56 days) but a steady state with 94%–96% retention was also reached after 7 d. R_d values are $>1 \cdot 10^3 \text{ L} \cdot \text{kg}^{-1}$ after 1 d of equilibration time (Table 3) in good agreement with the literature [9,14,44,49,51]. The influence of ionic strength on the retention of U(VI) in DGS is 3–5 pp lower than for Eu(III) and Sm(III), and especially compared to the adsorption of Cs(I). The solubility of U(VI) is controlled by CaUO_4 and $\text{Na}_2\text{U}_2\text{O}_7$ at $\text{pH} > 9$ [3,9,63]. The solubility limits are supposed to be 10^{-7} to $10^{-14} \text{ mol} \cdot \text{L}^{-1}$. In the present study, the precipitation of U(VI) after 7 d of equilibration was investigated (Figure 1). Only <13% of the initial U(VI) were immobilised which excludes precipitation as a retention mechanism on the short timescale. This agrees very well with the study of Tits et al. [9] who found a steady state for the retention of U(VI) on C-S-H phases ($\text{C/S} = 1.1$) after 10 d of equilibration time. They also observed a small decrease in R_d values for U(VI) with increasing salinity of the background electrolyte and no precipitation of CaUO_4 in the nanomolar concentration range. Tits et al. [9] also observed that U(VI) uptake increases with increasing C/S ratio or Ca(II) concentration. They explained this by the formation of a Ca-U-bearing solid but were not able to determine a solubility limit in their sorption isotherm experiments. Recent studies have shown that the initial retention mechanism for U(VI) in this study and probably also in the older study of Tits et al. [8] is surface complexation of $\text{UO}_2(\text{OH})_3^-$ or $\text{UO}_2(\text{OH})_4^{2-}$ most likely via Ca(II) bridges [30,55,56,78]. Ca(II) adsorbs on deprotonated silanol groups on the C-S-H phase's edge where a hydroxy ligand of U(VI) can be attached. Since the tobermorite structure is naturally saturated with

Ca(II) [79], the immobilisation of U(VI) can take place on a short timescale and is very effective. In the long term, precipitation or incorporation in the C-S-H phase's structure of U(VI) as described by Harfouche et al. [52] and Tits et al. [57] may also take place, leading to an almost irreversible retention behaviour.

Table 3. Distribution coefficients R_d for the retention of $5 \cdot 10^{-7}$ mol·L⁻¹ U(VI) on Circosil® in 0.1 M NaCl (pH 10.9) and diluted Gipshut solution (DGS, pH 10.6) at ten different sampling times (also in the presence of $5 \cdot 10^{-7}$ mol·L⁻¹ Sm(III), Eu(III), Cs(I), Zr(IV), Ru(III), Mo(VI) and Pd(II)).

Equilibration Time [d]	$R_d(\text{U(VI)})$ in 0.1 M NaCl [10 ³ L·kg ⁻¹]	$R_d(\text{U(VI)})$ in DGS [10 ³ L·kg ⁻¹]
0.04	0.34 ± 0.06	0.24 ± 0.09
1	1.8 ± 0.7	1.9 ± 1.4
3	5 ± 2.4	1.2 ± 0.1
7	19 ± 10	4.2 ± 1.1
14	71 ± 17	5.3 ± 3.2
28	71 ± 20	12 ± 12
56	19 ± 20	7 ± 4
112	2.8 ± 0.5	3.2 ± 0.7
168	110 ± 76	>100 *
217	210 ± 200	4 ± 2

*At least one of the triplicates was below the detection limit.

In 0.1 M NaCl, $2.8 \pm 1.2 \cdot 10^{-3}$ mol·L⁻¹ Ca(II) is leached out of Circosil® after 7 d in the presence of the WC. In DGS, the leaching is with $4.6 \pm 1.0 \cdot 10^{-3}$ mol·L⁻¹ Ca(II) more effective due to the amount of competing ions, e.g., Na(I), displacing Ca(II) from the C-S-H phase's surface. Older results on the influence of ionic strength on Ca(II) leaching from Portland cement show a similar trend, where in 0.1 M NaCl solution $3.0 \pm 0.1 \cdot 10^{-3}$ mol·L⁻¹ Ca(II) and in 2.5 M NaCl $3.8 \pm 0.1 \cdot 10^{-3}$ mol·L⁻¹ Ca(II) are leached out of the cement after 72 h [80]. Therefore, here, in DGS, less Ca(II) is accessible to form Ca-O-U-bridges and the retention of U(VI) decreases slightly. Nevertheless, there is still enough Ca(II) on the Circosil® surface left to immobilise the major part (>94%) of U(VI).

A comparison between the present study and a kinetic study on a wet chemical synthesised C-S-H phase (C/S = 1.08) shows similarities of the retention behaviour of U(VI) in DGS [14]. In that study, U(VI) retention increases fast and reaches a first steady state after 7 d. This contradicts literature where a higher C/S ratio leads to a lower U(VI) immobilisation [51] but is in good agreement with Tits et al. [9]. The retention of U(VI) is slightly slower at the higher C/S ratio in 0.1 M NaCl than in the current study [14]. This, again, agrees with the findings of Pointeau et al. [51]. It seems that decreasing U(VI) immobilisation with increasing C/S ratio is valid for low ionic strength but reverses at higher salinity. Ochs et al. [3] explained the decrease in U(VI) retention with increasing C/S ratio with Ca(II) occupying binding sites for U(VI) but the results in DGS and in the literature [30,55,56] show that the presence of Ca(II) enhances the immobilisation of U(VI). The decrease may be caused by the increasing OH⁻ concentration somehow interfering with the U(VI) retention on the C-S-H phase's surface. Another explanation could be the formation of a Ca(II)-U(VI) species in solution before the immobilisation takes place. This takes the decreasing immobilisation of U(VI) with increasing C/S ratio into account as well as the increasing immobilisation in the presence of Ca(II) in solution.

It is remarkable that three different kinetic studies on U(VI) and Eu(III) show different adsorption kinetics comparing both elements. Burešová et al. [44] noticed a faster immobilisation of Eu(III) than U(VI). Baur et al. [14] observed retention on the same timescale and, in the present study, U(VI) becomes immobilised faster than Eu(III). The main difference is the time Eu(III) needs to reach a steady state. With more competing ions present in solution, Eu(III) needs more time for immobilisation. This is firstly a direct hint of a retention mechanism for Eu(III) where competing ions play a role, e.g., adsorption or

incorporation. Secondly, it indicates the necessity of investigating element mixtures instead of solely single-element studies.

4. Conclusions

This study shows that the retention of the investigated elements on the commercial and hydrothermal synthesised C-S-H phase Circosil[®], which is stable against CO₂, is comparable with the retention on wet chemical synthesised C-S-H phases. This is shown by the obtained R_d values. To the best of our knowledge, this is the first time the retention behaviour of eight repository relevant elements combined as a WC was studied, especially under alkaline and high-saline conditions. Additionally, this time-dependent study delivers new findings on the retention mechanisms in the nanomolar concentration range.

For Cs(I), discrepancies between commercial and wet chemical synthesised C-S-H phases can be seen, e.g., compared to the similar study of Baur et al. [14]. But there are many contradicting studies concerning the adsorption of Cs(I) on C-S-H phases in the literature. Many factors can possibly influence the Cs(I) retention: C/S ratio, amorphousness, reversibility of the adsorption process, solid-to-liquid ratio, salinity and competing ions. Under the used conditions, moderate and irreversible uptake of Cs(I) on Circosil[®] could be shown in 0.1 M NaCl ($75 \pm 1\%$). The adsorption is with $14 \pm 1\%$ lower in DGS and decreases slowly after 112 d. Unfortunately, a direct impact of the WC elements was not visible due to the highly saline background electrolytes. A direct comparison between single-element and WC experiments or additional studies in lower-saline solutions or with higher concentrations of the competing ions are necessary to elucidate the pure influence of the radioactive inventory in HLW disposal.

The present study proves that precipitation (e.g., as Na₂U₂O₇ or CaUO₄) can be excluded as initial retention mechanism for U(VI) on Circosil[®] in the nanomolar concentration range. Competing ions from the WC itself or from the background electrolytes only slightly influence the strong and irreversible retention. Compared to the literature, the role of the C/S ratio, Ca(II) concentration and pH value in the immobilisation kinetics needs further investigation.

The preferred retention of Sm(III) and Eu(III) on Circosil[®] over precipitation and wall adsorption could clearly be seen. The wall adsorption decreased from >90% in 0.1 M NaCl and >60% in DGS to <15% in the presence of the C-S-H phase. Combined with the findings of the kinetic study where increasing salinity leads to decreasing retention of Sm(III) and Eu(III), it can be concluded that surface complexation is the initial immobilisation mechanism for both elements. Furthermore, the slower kinetics compared to previous studies suggests a competing effect, e.g., between Eu(III), Sm(III) and Ru(III). A concentration series can be useful for further clarification.

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3.1.2 Sorption experiments as efficient as possible: Mini-column experiments (MCE) using HPLC-ICP-MS coupling with a new data analysis approach to determine sorption parameters

This research paper was submitted to “Microchemical Journal” on 30 April 2024 and was online available on 24 August 2024 (<https://doi.org/10.1016/j.microc.2024.111511>). The authors are Aaron Haben, Kristina Brix, Nico Bachmann and Ralf Kautenburger. The respective contributions of the authors to this work are listed in accordance with the CRediT standard in Table 4. The graphical abstract to this publication is shown in Figure 21.

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Table 4: Author contribution roles for the publication "Sorption experiments as efficient as possible: Mini-column experiments (MCE) using HPLC-ICP-MS coupling with a new data analysis approach to determine sorption parameters" in form of the CRediT standard [12].

Contributor roles	Author(s)
Conceptualisation	Aaron Haben, Ralf Kautenburger
Methodology	Aaron Haben
Validation	Aaron Haben, Kristina Brix
Formal analysis	Aaron Haben
Investigation	Aaron Haben, Nico Bachmann
Writing – original draft	Aaron Haben
Writing – review and editing	Aaron Haben, Kristina Brix, Ralf Kautenburger
Visualisation	Aaron Haben, Nico Bachmann
Data curation	Aaron Haben
Supervision	Ralf Kautenburger
Project administration	Ralf Kautenburger
Funding acquisition	Ralf Kautenburger

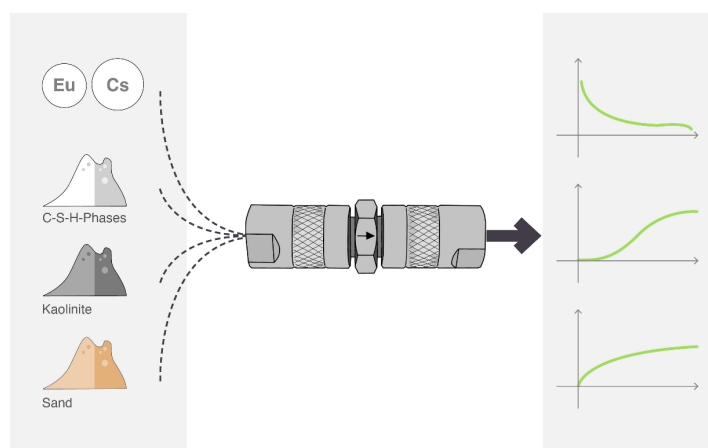


Figure 21: Graphical abstract to the publication "Sorption experiments as efficient as possible: Mini-column experiments (MCE) using HPLC-ICP-MS coupling with a new data analysis approach to determine sorption parameters " [12].

Extended abstract:

Usually, to determine retention and sorption parameters, diffusion, batch or conventional column experiments are conducted. However, these methods often do not fully reflect realistic conditions, are time-consuming and/or material intensive. The newly developed MCEs represent a promising, resource-efficient approach in which dynamic retention parameters can be determined under realistic conditions (e.g. S/L ratios), in a resource-efficient and fully controllable manner. The aim of this work was the development and application of a highly efficient MCE method using an HPLC system and its coupling to an ICP-QQQ for the quantification of the retention behaviour of repository-relevant elements on also repository relevant construction and backfill materials. This method enables ultra-fast sorption experiments (5 to 67 h depending on the experiment), whereby only 100-150 mg adsorbent and approx. 160 mL eluent are required.

Another focus of the work was the presentation of a new data evaluation strategy to derive dynamic R_d values and $q_{\max}$. For this purpose, the MCE method was applied to sorption studies of the repository-relevant elements Cs(I) and Eu(III) on the commercial C-S-H phase Circosil®, the clay mineral kaolinite and quartz sand. These materials are all relevant for possible barriers in a potential HLW repository in northern Germany.

The MCEs were conducted using HPLC guard columns (mini columns) filled with the respective adsorbents. Either a 10 mM or 100 mM NaCl solution was used as eluent. Two different methods were used to quantify the retention parameters. In one case, retention parameters of Eu(III) on kaolinite and quartz sand were determined using HPLC-ICP-QQQ coupling. Here, the eluate was fed into the ICP-QQQ via a split flow valve (SFV) with additional online dilution. In another case, MCEs were conducted in combination with a fraction collector. Due to the strong leaching of Si(IV) and Ca(II) from the Circosil® and the associated high ionic strength, coupling is not applicable for the analysis of C-S-H phases. During the experiment the whole eluate was collected using a fraction collector and then prepared (diluted) for the ICP-QQQ analysis. This approach was used to determine the retention parameters of Cs(I) on Circosil®.

Due to the known instability and leaching of the C-S-H phases, consideration of their mass loss (over the duration of the experiments) was essential for the correct calculation of the sorption parameters. For this purpose, additional MCE leaching studies were conducted, which showed reproducible leaching of Ca(II) and Si(IV) at a constant pH of 10.7. The observed ratio of leached Si(IV) and Ca(II) suggests a low C/S ratio of the Circosil® used (approx. 0.65). Based on the measured Ca(II) and Si(IV) concentrations in the eluate, a linear regression model for the percentage mass loss as a function of the eluent volume was developed and integrated into the sorption models. These are the Freundlich- and Langmuir isotherms and the Thomas model for fitting breakthrough curves.

In the MCE studies with Cs(I) on Circosil®, retention was drastically reduced at the higher ionic strength (100 mM NaCl). The $q_{\max}$ decreased from 4.82 mg g^{-1} (10 mM NaCl) to 2.65 mg g^{-1} (100 mM NaCl). In those MCE, the R_d values ($\log R_d$) 213 L kg^{-1} (2.33) in the lower ionic strength and 318 L kg^{-1} (2.50) in the increased ionic strength were determined. This trend is due to the competition of Na^+ ions with Cs^+ for the sorption sites, especially ion exchange, and is consistent with literature. The MCE Thomas model fit ($R^2 = 0.991\text{--}0.992$) and Freundlich isotherm ($R^2 = 0.939\text{--}0.995$) obtained from these MCEs correlated best with experimental data. The good fit by the Freundlich model indicates reversible sorption in the form of multilayer adsorption at heterogeneous sorption sites and the Thomas model provided the most reliable $q_{\max}$ values. For validation, the R_d values determined via MCE were compared with those from batch experiments and showed very good agreement (162 L kg^{-1} (2.21) and 282 L kg^{-1} (2.45)). An additional literature comparison also showed good agreement.

In the MCE coupling experiments, Eu(III) shows a high retention on the kaolinite/sand mixture, whereby the BTC again correlates very well with the Thomas model ($R^2 = 0.983\text{--}0.997$). In general, the kinetics of the Thomas model are assumed to be homogeneous pseudo-second-order adsorption, in which axial dispersion can be neglected. Due to the very good correlation, this results in the conclusion to be the case for the Eu(III)-adsorption on kaolinite and sand. The reason for the high retention is the trivalency of Eu(III), which in turn leads to a strong electrostatic attraction on the negatively charged surfaces of the kaolinite. Furthermore, the $q_{\max}$ values of Eu(III) determined in the MCE agreed very well with the values from the literature. The determined $q_{\max}$ of 0.52 mg g^{-1} on kaolinite deviated from the literature value by only 11% and the $q_{\max}$ of 0.09 mg g^{-1} was identical.

To summarise, in this work a highly efficient and validated method for the determination of sorption parameters using MCE was successfully developed. The consideration of the mass loss of the adsorbent by the new data evaluation strategy enabled the reliable determination of sorption parameters on unstable materials such as C-S-H phases. Furthermore, an additional stage of the method using the MCE-HPLC-ICP-QQQ coupling was developed and validated for the investigation of more stable adsorption materials. Overall, the MCE method is faster, more material efficient and more accurate than conventional methods. It offers a powerful tool for the investigation of retention processes under dynamic conditions and is of great advantage for safety assessment in repository research. The results were confirmed by a very good agreement with three different adsorption models and established batch experiments.



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Sorption experiments as efficient as possible: Mini-column experiments (MCE) using HPLC-ICP-MS coupling with a new data analysis approach to determine sorption parameters

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ABSTRACT

To quantify retention and sorption parameters, diffusion-, batch- or column experiments are common practice. However, these are either not close to nature, extremely time-consuming or material intensive. A promising approach to eliminate these problems is the performance of mini-column experiments (MCE). Due to dynamic retention and realistic solid-liquid ratios, these are close to nature and resource-efficient. The aim of this work is to perform highly controllable MCE using a HPLC (high-performance liquid chromatography) system and HPLC-ICP-MS (inductively coupled plasma mass spectrometry) coupling. With this approach, ultra-fast sorption experiments are possible only using 100–150 mg adsorbent and 160 mL eluent. That means, sorption experiments are even more time- and cost-efficient and also more controllable than with conventional methods. The presented method is based on a newly developed MCE-HPLC-ICP-MS coupling, which was applied to investigate the sorption of Eu(III) on kaolinite and sand in 10 mM NaCl. With that it was possible to carry out dynamic sorption experiments in just 5–15 h and thus determine e.g. maximum loading capacity ($q_{\max}$) in a very short amount of time. Furthermore, a quantification method for eluates of high ionic strength is presented. Here, the sorption of Cs(I) on calcium silicate hydrate (C-S-H) phases in 10 mM and 100 mM NaCl was investigated. For validation, the sorption distribution ratios (R_d) obtained were compared with those from batch experiments. These agreed very well with each other and with those from the literature. Overall, with MCE more sorption parameters can be determined much faster, more accurately and more efficient than with the conventional methods.

1. Introduction

To investigate the retention behaviour of different substances on multiple adsorption materials, the most common method used are batch sorption experiments. Here one or multiple test series with a set of many individual samples are investigated under precisely defined conditions. This enables the determination of simple sorption parameters, like distribution coefficients (K_d values) as a function of the test parameters used [1–6]. However, batch experiments are, due to the unrealistic solid-liquid ratios and static equilibrium, not as close to nature as other experimental setups. Two other (common) methods to investigate or determine retention parameters are diffusion and column experiments. These are predominantly close to nature but are also either very time-consuming and/or material intensive [7,8].

A few years ago, initial attempts were made to develop a more efficient and realistic method for carrying out sorption experiments. The

idea was to fill real mini-columns with adsorbent material and carry out mini column experiments (MCE) using high-performance liquid chromatography (HPLC) devices [8–10]. With such an experimental setup, in theory only 50–300 mg of adsorbent and less than 300 mL of eluent are required. But, until now, there has been no valid MCE method to describe sorption processes or to calculate chemical-physical sorption parameters. In this work we present a new MCE method that can be used to derive dynamic sorption distribution ratios (R_d) and maximum loading capacities ($q_{\max}$) for mono- and higher-valent metal ions on strongly sorbing solid phases. With this method, various adsorbents (calcium silicate hydrate phases, kaolinite and sand) are compacted in mini-columns (100–150 mg) and connected to the HPLC to analyse the retention behaviour of Cs(I) and Eu(III) as strongly sorbent metal ions under precisely defined conditions. Cs(I) was selected as the first analyte to test the MCE method because it is only present as $\text{Cs}_{(\text{aq})}^+$ over the entire pH range of 2–14 and it does not precipitate under natural conditions

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[11–13]. This simplifies the investigations at the beginning, as no further retention effects are to be expected apart from adsorption. After optimising the method, the trivalent Eu(III) was also selected, which shows strong retention effects (in addition to sorption and precipitation) and is used in the MCE as a less toxic and non-radioactive homologue for Cm(III) and Am(III) [14–16]. The retention was quantified either via a newly developed HPLC-ICP-MS (inductively coupled plasma mass spectrometry) coupling or by means of a fraction collector and subsequent ICP-MS measurement. Regarding the HPLC-ICP-MS coupling, also a new data evaluation is presented here.

All adsorption materials investigated in this study are components of possible barrier materials for a potential repository for high-level nuclear waste (HLW) in Germany [17]. The most dangerous components of HLW are enriched uranium from the nuclear fuel elements and its fission products, such as Cs(I) or Eu(III), whereas Eu(III) also acts as homologues to Sm(III), Am(III) and Cm(III) [13–16,18]. Due to their chemical and radiotoxic properties, a hypothetical exposure of these radionuclides in the environment would thus have a permanently damaging effect on humans and nature. To effectively protect future generations from the harmful effects of radionuclides, the final storage of HLW in deep geological formations is envisaged [17,19–21].

For Germany a storage in geological host rock formations at depths of 250–1000 m using natural and artificial barriers (multi-barrier system) is planned. This consists of the HLW-containing castor casks, cement-based materials, which are used as construction, closure and/or backfill materials, further backfill in and around the area used for final disposal (most likely clay based materials) and the geological formation in which the waste is emplaced (the host rock) [1,17,19,20]. As a result, the investigation of the retention behaviour of repository-relevant elements or element mixtures under different geochemical conditions in cement-based materials, their alteration products and clay minerals are of great interest. But solutions in equilibrium with hydrated cement are hyperalkaline and the minerals are not thermodynamically stable in contact with penetrating water and tend to corrode over time. This results in cement aging phases, which consist essentially of calcium silicate hydrate (C-S-H) phases and form solutions with pH values between 10 and 13. Since both freshly hydrated and aged cement consist mainly of C-S-H phases and these are considered to be responsible for the heavy metal binding ability of cementitious materials, they are a central component of risk assessment in current repository research and are also investigated in this work [4,22–24]. Another, more stable, adsorbent material used in this study is kaolinite, which is one of the most common clay minerals and the simplest among the aluminosilicate clays [25]. Therefore, kaolinite is ideal as a simple model for clay minerals as a possible geotechnical barrier.

During the MCE, the analytes are injected into the eluent and with that onto the column. After subsequent analysis of the eluate using ICP-MS, the retention behaviour can then be determined and retention parameters calculated. For kaolinite as adsorbent material, direct quantification can be carried out via HPLC-ICP-MS coupling. However, at present, the ionic strength of the eluate is a limiting factor for quantification via HPLC-ICP-MS coupling. Since C-S-H-phases tend to leach in aqueous media, high concentrations of Ca(II) and Si(IV) ions are to be expected and a workaround of the coupling must be investigated in advance [26,27]. For this case of excessive leaching, an alternative method is also presented in this work. Hereby, the eluate is collected by means of a fraction collector and, after subsequent processing, the fractions are also analysed using ICP-MS. In addition, this experimental approach also allows a more detailed investigation of the leaching behaviour itself.

2. Materials and methods

2.1. Chemicals

Ultrapure water ($0.055 \mu\text{S cm}^{-2}$) (PURELAB® Chorus 1 ultrapure

water filtration unit, Elga LabWater, High Wycombe, UK) was used to prepare all solutions. NaCl with premium-grade quality (EMSURE®) from Merck (Darmstadt, Germany) was used to prepare the eluents for MCEs and the electrolytes for the batch experiments. A solution with 10 mg L^{-1} of Sc(III) ($1,000 \text{ mg L}^{-1}$ in 5 % HNO_3 , Alfa®, Karlsruhe, Germany) and Ho(III) ($1,000 \text{ mg L}^{-1}$ in 2–3 % HNO_3 , Merck Certipur®, Darmstadt, Germany) in ultrapure water was prepared as the internal standard stock solution for all ICP-MS measurements. HNO_3 (Rotipuran® Supra 69 %, Carl Roth, Karlsruhe, Germany) was used to acidify the measurement solutions, whereas HCl (HCl 30 % Suprapur®, Merck Supelco®, Darmstadt, Germany) and NaOH (Suprapur® 30 %, Merck, Darmstadt, Germany) were used to adjust the pH in the experiments. Argon 5.0 (Ar $\geq 99.999 \text{ mol\%}$, ALPHAGAZ™ 1 Argon, Air Liquide, Düsseldorf, Germany) was used as plasma gas for ICP-MS measurements. For the experiments and ICP-MS calibration, Cs(I) ($1,000 \text{ mg L}^{-1}$ in 2.5 % HNO_3 , AccuStandard, New Haven, USA) and Eu(III) ($10,000 \text{ mg L}^{-1}$ in diluted HNO_3 , Agilent, Kingstown, USA) ICP-MS standard solutions were used. Furthermore, Ca(II) ($1,000 \text{ mg L}^{-1}$ in 0.5 mol L^{-1} HNO_3 , Merck Certipur®, Darmstadt, Germany) and Si(IV) ($10,000 \text{ mg L}^{-1}$ in water, Tr. HF, AccuStandard, New Haven, USA) standards were used for ICP-MS calibration of the leaching experiments.

The used C-S-H phase is commercially available Circosil® 0.1 from Cirkel (Emsdetten, Germany). Cirkel states for the Circosil® structure that it consists of 88 % tobermorite phases ($5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$) and 10 % embedded SiO_2 . With this information and additional XRF-data (X-ray fluorescence spectroscopy) provided by Cirkel, a molar Calcium to Silicon ratio (C/S) of approx. 0.65 can be calculated. However, if only the tobermorite part is used as a basis for calculation, the C/S ratio would be 0.83 [28,29]. For the MCE with HPLC-ICP-MS coupling a mixture of kaolinite KGa-1b (Georgia, USA), sold by the Clay Minerals Society (Chantilly, USA) and quartz sand (purified sea sand, Merck, Darmstadt, Germany) were used as stationary phases in the column.

2.2. Preparing the mini columns

The mini columns used are HPLC guard columns (UPC-130B, UPCHURCH SCIENTIFIC™, Oak Habor, USA); either in factory condition (2 mm ID) or drilled out to 3.5 mm ID. In addition, two different filter discs were used: one with a pore size of 500 nm (A-103X, UPCHURCH SCIENTIFIC™, Oak Habor, USA) and one with a pore size of 100 nm (Stainless steel filter disc, Applied Research Europe, Berlin, Germany). To guarantee impermeability using the stainless-steel filter disc (SSFD), a strip of parafilm approx. 1–2 mm wide and approx. 70 mm long was wrapped around it before it was installed in the column. To fill the column, it was clamped in a vice, the dry adsorbent was filled into the column with a suitable funnel and thereby gradually compacted.

2.3. MCE without coupling

The HPLC components used are Agilent 1100 and 1200 HPLC systems (Walldbronn, Germany) and listed in Table 1.

The MCE were performed with 10 mM or 100 mM NaCl as eluent and at 25 °C column temperature. For both, the 3.5 mm ID columns were packed with Circosil® (150.1 mg for the experiment with 10 mM NaCl and 152.1 mg for the one with 100 mM NaCl), sealed with the SSFD and then preconditioned in the HPLC for 150 min using a flow gradient from 10 to $40 \mu\text{L min}^{-1}$. After preconditioning the flowrate (Q) of the eluent was set to $40 \mu\text{L min}^{-1}$. In advance to the experiments the Cs(I) ICP-MS standard solutions were neutralised with NaOH each and used for injection. Therefore, the concentrations of the injection solutions were 948.2 mg/L and 959.0 mg/L for the MCE in 10 mM and 100 mM NaCl. For each experiment 100 times $12.47 \mu\text{g}$ (in 10 mM NaCl) or $9.48 \mu\text{g}$ (in 100 mM NaCl) of Cs(I) were injected into the eluent in 38 min intervals (97.8 or 75.3 nmol Cs(I) per injection). Behind the column, the entire eluate was collected by means of a fraction collector. Samples were taken from the individual fractions for an ICP-MS measurement and the

Table 1

Components and software of used HPLC system in MCE without coupling.

Hardware:
1100 Series G1379A Degasser
1100 Series G1312A Binary Pump
1100 Series G1313A ALS
1100 Series G1316A Colum
1100 Series G1315B DAD
1200 Series G1364C Analyte FC
Software:
ChemStation for LC 3D Systems Rev. B.02.01-SR2 [260]

pH values were determined (pH-meter SevenMulti, pH-electrode InLab®, Mettler Toledo, Columbus, USA). For the ICP–MS measurement, an Agilent 8900 ICP–QQQ (Santa Clara, USA) with an Agilent SPS 4 autosampler (Santa Clara, USA) was used. Therefore, 20 μL of the fractions were added to 9.67 mL Milli-Q water, 300 μL HNO_3 (69 %) and 10 μL internal standard stock solution. The measurement was performed with different cell gas modes: ^{28}Si and ^{40}Ca were measured in H_2 mode via mass pair (Q_1 , Q_2) = (28, 28) and (Q_1 , Q_2) = (40, 40) and ^{133}Cs in “NoGas”-mode. An external calibration was done for quantification.

2.4. Leaching of C-S-H phases

Since C-S-H phases are known for their strong leaching behaviour, it can be assumed that the mass of Circosil® in the column is not constant during one experiment [26,27]. Most of the calculations described in chapter 2.7 require the exact mass of the adsorbent material. This is why leaching studies were performed. Hereby multiple MCE with the 3.5 mm ID column and different experimental conditions were performed (described in Table 2). In all cases, Q was 40 $\mu\text{L min}^{-1}$ and the column temperature was again 25 °C. To simulate Circosil® at a late stage in the experiment, i.e., already leached Circosil®, two of the four samples were treated (washed) in advance. Therefore 24.17 g of Circosil® were weighed out and then suspended 8 times with ultrapure water, stirred and decanted. Afterwards, the suspension was filtered through a suction flask and filter paper with a pore size of 7 μm and washed again 8 times with ultrapure water. The remaining solid was then dried to constant weight (7 days) at 110 °C to give 19.57 g of washed Circosil®. All filled columns were preconditioned using the same flow gradient as described in chapter 2.3.

The eluate was collected in the fraction collector and afterwards the pH values, the Ca(II) - and the Si(IV) -concentration in the fractions were determined. To quantify the leached Ca(II) - and Si(IV) -concentrations, ICP–MS measurements were performed analogue to the MCE described in chapter 2.3.

2.5. Batch experiments

For the batch experiments, 10 mL of either 10 mM or 100 mM NaCl solution was added to 40 ± 0.2 mg Circosil® ($\text{S/L}=4$ g/L) in a 15 mL polypropylene (PP) centrifuge tube (Ultra-High Performance Centrifuge

Tube, VWR® International, Darmstadt, Germany), followed by equilibration in a horizontal shaker (Promax 1020 platform shaker, Heidolph Instruments, Schwabach, Germany) at room temperature for 7 days. This resulted in a pH value of 10.7 for all samples (analogue to the MCE, see chapter 3.1 and 3.2). Cs(I) was then added at concentrations of 0, 0.5, 2.5, 10, 50, 250, 1,000, 5,000, 25,000, 50,000 $\mu\text{g/L}$ and then again shaken for 7 d. For better statistical evidence, all samples were prepared in triplicates. Phase separation was carried out in a centrifuge (Centrifuge 3-18KS, Sigma, Osterode am Harz, Germany) at 16,990 g for 30 min at 21 °C. Then 10 μL to 1 mL of the supernatant solution (depending on dilution) was taken and the ICP–MS measurement solutions were prepared analogue to chapter 2.3. Quantification of Cs(I) was performed as described in chapter 2.3.

2.6. MCE with HPLC-ICP-MS coupling

Here the HPLC components used are Agilent 1260 Infinity II HPLC systems (Waldbronn, Germany) and listed in Table 3.

The HPLC system was coupled to the ICP–MS (Agilent 8900 ICP–QQQ, Santa Clara, USA) via a PEEK capillary (1/16" x 0.13 mm ID, nature with red stripes, ERC, Riemerling, Germany) and a split-flow-valve (SFV; UP P-451, Flow-Splitter, Upchurch Scientific, Oak Harbor, USA). The experimental setup is schematically shown in Fig. 1.

For the experiments the 2 mm ID column was packed with either 102.5 mg sand or 104.4 mg of a 1:9 wt% kaolinite/sand mixture. In this case, the columns were sealed with the A-103x filter disc. The columns were preconditioned with a flow gradient from 10 to 100 $\mu\text{L min}^{-1}$ for 120 min. A 10 mM NaCl solution with a flow rate of 100 $\mu\text{L min}^{-1}$ was used as eluent and a column temperature was again set to 25 °C. The split of the SFV was set to approximately 1:7.5 (13.3 % of the flow goes to the ICP–MS). To increase the flow to the nebuliser, an internal standard solution containing 5 % HNO_3 , 1 ppb Sc and 1 ppb Ho was introduced via the Peri Pump (0.2 rps) through a T-piece. During the experiments 5 μL of an Eu(III) solution with a concentration of either 70 mg/L (on sand; 2.30 nmol Eu(III) per injection) or 100 mg L^{-1} (on kaolinite/sand mixture; 3.29 nmol Eu(III) per injection) were injected. The ICP–MS quantification was carried out using a time-resolved (TRA) measurement method.

To provide initial validation of the HPLC-ICP–MS coupling, another MCE was performed with Eu(III) on a kaolinite/sand mixture using the method with fraction collector described in section 2.3. Here 375.3 mg of the 3:7 wt% kaolinite/sand mixture was packed in the 3.5 mm ID column and 5 μL of a 700 mg/L Eu(III) solution (23.0 nmol per injection) was injected multiple times into 10 mM NaCl. Quantification was also performed as described in chapter 2.3.

2.7. Data evaluation of MCE

To quantify the retention behaviour of the analytes the total recovery (R) in % gets calculated as shown in equation (1).

$$R = \frac{C_0}{C_{eq}} \cdot 100\% \quad (1)$$

Table 2

Leaching MCE and their experimental conditions.

MCE	Adsorbent	Filter disk	Eluent	Injection
L 1	Circosil®	A-103x	10 mM NaCl	5 μL ultrapure water
L 2	Circosil® washed	SSFD	100 mM NaCl	5 μL ultrapure water
L 3	Circosil® washed	SSFD	10 mM NaCl	5 μL of 500 mg/L Cs(I) -solution
L 4	Circosil®	A-103x	10 mM NaCl	5 μL of 500 mg/L Cs(I) -solution

Table 3

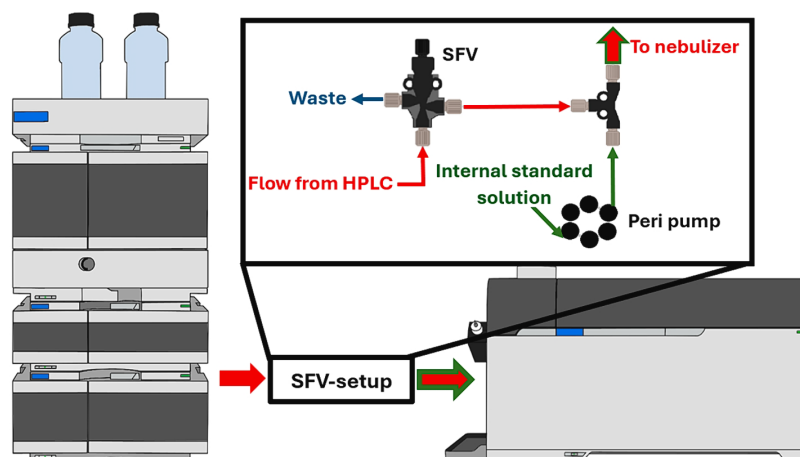
Components and software of used HPLC system in MCE with HPLC-ICP-MS coupling.

Hardware:

1260 Infinity II G7111B Quat Pump
 1260 Infinity II G7129A Vialsampler
 1260 Infinity II G7116A MCT
 1260 Infinity II G7117C DAD HS

Software:

OpenLab CDS ChemStation Edition Rev. C.01.10 [322]

**Fig. 1.** Schematic diagram of the HPLC-ICP-MS coupling used for the MCE (SFV, split-flow-valve).

Since the MCE analysis performed are injection-based the initial analyte concentration C_0 [mg/L] must be calculated as shown in equation (2), whereas the equilibrium concentration C_{eq} [mg/L] is the not immobilised amount in the liquid phase which is measured via ICP-MS.

$$C_0 = \frac{C_{in} \cdot V_{in}}{Q \cdot t} \quad (2)$$

In equation (2) C_{in} [mg/L] is the concentration of the injection solution, V_{in} [mL] the injection volume, Q [mL min⁻¹] the flowrate of the eluent and t [min] the time between each injection.

An other widely used method to quantify the retention is to calculate the sorption distribution ratio R_d [L kg⁻¹] (or $\log(R_d)$) shown in equation (3). The parameter q [mg g⁻¹] (in equation (3) [mg kg⁻¹]) is the loading of the analyte onto the adsorbent.

$$R_d = \frac{q}{C_{eq}} \quad (3)$$

Especially in the context of the MCE, where a large amount of data, like break through curves (BTC), are generated, the possibility to fit the experimental data with model calculations is particularly interesting. Two of the simplest sorption models are the Freundlich (equation (4)) and Langmuir (equation (5)) isotherms. Here K_F [L g⁻¹] is the Freundlich coefficient, n the Freundlich exponent, K_L [L g⁻¹] die Langmuir coefficient and q_{max} [mg g⁻¹] the maximal loading capacity of the analyte onto the adsorbent. The Freundlich isotherm assumes multilayer adsorption on heterogeneous surfaces (sorption sites of different strengths), with the adsorption energy increasing exponentially with the amount of adsorption sites. Furthermore, the interaction between dissolved molecules/adsorptive and non-uniform distribution of adsorption heat on the surface is also considered. Therefore, it can be assumed that the stronger sorption sites are occupied first, and the binding strength decreases as the sorption sites are occupied. Unlike the Langmuir

isotherm, no q_{max} is defined here and is therefore more applicable to problems with low to medium concentrations [30–32]. The Langmuir sorption model, on the other hand, is based on the assumptions that adsorption occurs at energetically equivalent sorption sites, that the maximum amount of adsorbate (adsorptive bound to the adsorbents) cannot be higher than the available sorption sites (formation of a monolayer) and that there is no interaction between the dissolved molecules/adsorptive [32–34].

$$q = K_F \cdot C_{eq}^n \quad (4)$$

$$q = q_{max} \cdot \frac{K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \quad (5)$$

Since Freundlich and Langmuir are comparatively simple models, the calculations were extended to include a fixed bed model. Due to its simplicity, the BTCs were fitted with the Thomas model (shown in equation (6)).

$$\frac{C_{eq}}{C_0} = \frac{1}{1 + \exp \left[\frac{K_{TH}}{Q} \cdot (q_{max} \cdot m - C_0 \cdot V_{Eff}) \right]} \quad (6)$$

In equation (6) K_{TH} [mL mg⁻¹ min⁻¹] is the Thomas constant, m [g] the mass of adsorbent material inside the column and V_{Eff} [L] the effluent volume which has passed the column. The Thomas model is one of the most used models for representing the influence of adsorption parameters on the breakthrough of an analyte in a column system. It assumes reversible Langmuir kinetics of pseudo-second order, whereas axial dispersion is neglected [35–40].

3. Results and Discussion

3.1. Leaching of C-S-H phases

As the exact mass of the adsorbent is required, conducting leaching studies are essential as a first step for the data evaluation of the MCE. Fig. 2 shows the leached Ca(II)- and Si(IV)-concentrations of the four C-S-H phase leaching experiments (denoted as L1–L4 in Table 2) as well as the pH values. The results show that there is almost no relevant difference in the leaching behaviour between each experiment. With that it can be assumed that the ionic strength of the eluent (within the observed boundaries), the used filter disc and the injected medium show no influence on the leaching behaviour. It could therefore be shown that a reproducible leaching of the Circosil® is accomplished independent of the test parameters. The only variable that leads to a slight change in leaching behaviour is the pre-treatment (washing) of the Circosil®. When using the washed Circosil® (L2 and L3), comparatively more Ca (II) was leached in comparison to the untreated Circosil®. Considering the pH, the same pH of 10.7 was measured for all four experiments, which corresponds very well with the literature [23,26].

The literature also describes that systems of high initial C/S ratios (>1) preferably leach Ca(II). But when the C/S ratio decreased to approx. 0.8 the C-S-H phases dissolve congruently. On the other hand, C-S-H phases with C/S < 0.8 preferably leach Si, again till they reach a C/S of 0.8 [26,27]. Assuming Circosil® has a C/S of approx. 0.65, the leached amounts of Ca(II) and Si(IV) (Fig. 2) fit the literature very well. Initially, significantly more Si(IV) (about 2.5 mmol/L) is released than Ca(II) (about 1 to 1.5 mmol/L), whereas later, equal amounts of Ca(II) and Si(IV) are released. The leaching behaviour of the washed Circosil® and the higher Ca(II) content leached also agrees very well with this observation. If, as already mentioned, more Si(IV) is initially leached at a C/S of about 0.65, the washing pre-treatment would increase the C/S. Accordingly, a higher Ca(II) concentration in the fractions would be expected in the leaching experiment. Irrespective of the slightly different Ca(II) concentrations in the fractions, the C/S in all fractions reach a value of approx. 1 after an eluent volume of 70 mL. The C/S in the remaining solids was not determined at this point but based on G. M. N. Baston et al. (2012) and A. W. Harris et al. (2002), a C/S in solution of 1

indicates a C/S in the solid of 0.8 due to the homogeneous dissolution of the C-S-H phase [22,26,27].

As mentioned, the exact mass of the adsorbents must be known for the calculations (see chapter 2.7), and any mass loss due to leaching must be considered. Furthermore, it has been shown that a reproducible leaching of Circosil® is ensured independent of the test parameters. Therefore, a simple model for the leaching could be developed. For each analyte measured the concentrations shown in Fig. 2 were averaged. Based on the averaged Ca(II) and Si(IV) concentrations, the corresponding leached oxygen concentrations were calculated using two different approaches: The first approach, shown in equation (7), is based on a tobermorite structure (cf. chapter 2.2) and for the second one, shown in equation (8), the oxygen concentration was calculated based on the precursors for C-S-H phases syntheses in laboratory scale; CaO and SiO₂ [41,42]. The *n* in equation (7) and (8) refers to the molar number of the elements.

$$n(O) = \frac{\left(\frac{17}{5} \cdot n(Ca) + \frac{17}{6} \cdot n(Si)\right)}{2} \quad (7)$$

$$n(O) = n(Ca) + 2 \cdot n(Si) \quad (8)$$

The results from equation (7) and (8) were averaged again. To determine the total mass loss, all averaged contents of O, Si, and Ca were then added. From this, the percentage loss could then be determined, plotted against the effluent volume and from this, by linear regression, the calculation basis for the mass loss depending on the effluent volume could be gained. The fit line of the linear regression is given as equation (9) ($R^2 = 0.996$).

$$massloss[\%] = 1.10154 + 0.0532 \cdot V_{eff} \quad (9)$$

With equation (9), the Circosil® mass loss as a function of effluent volume can be considered in the Freundlich isotherm (Eq. (4)), Langmuir isotherm (Eq. (5)) and Thomas model (Eq. (6)). Doing so, those models rewrite as equation (10), (11) and (12):

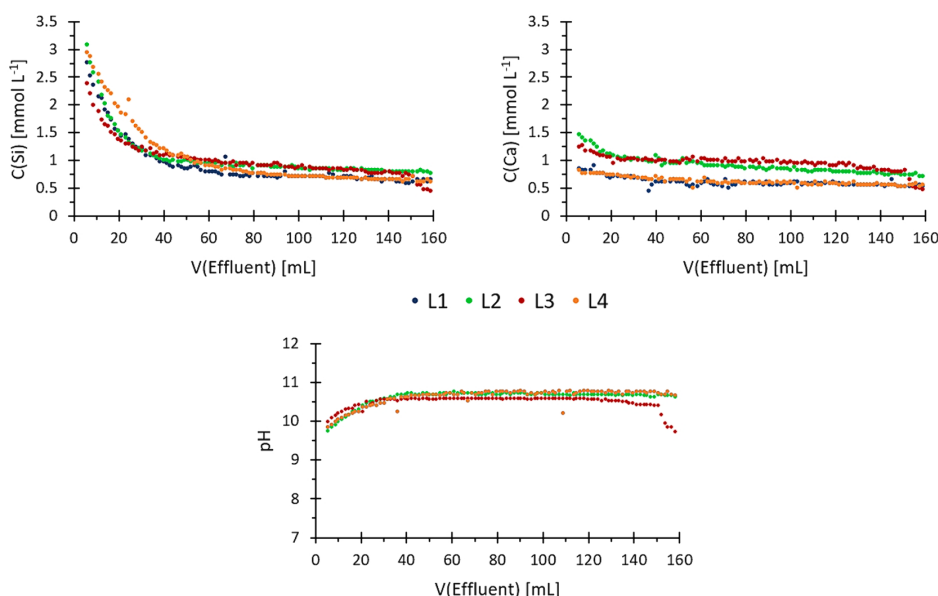


Fig. 2. Measured pH values, Ca and Si contents of the fractions in the individual leaching experiments (according to Table 2. L1 Circosil® in 10 mM NaCl, L2 washed Circosil® in 100 mM NaCl, L3 washed Circosil® in 10 mM NaCl, L4 Circosil® in 10 mM NaCl) plotted against the effluent volume.

$$q = \frac{m_{\text{sorb}}}{m_0 - \left(m_0 \left(\frac{0.0532 \cdot V_{\text{eff}} + 1.10154}{100} \right) \right)} = K_F \cdot C_{\text{eq}}^n \quad (10)$$

$$q = \frac{m_{\text{sorb}}}{m_0 - \left(m_0 \left(\frac{0.0532 \cdot V_{\text{eff}} + 1.10154}{100} \right) \right)} = q_{\text{max}} \cdot \frac{K_L \cdot C_{\text{eq}}}{1 + K_L \cdot C_{\text{eq}}} \quad (11)$$

$$\frac{C_{\text{eq}}}{C_0} = \frac{1}{1 + \exp \left[\frac{K_{\text{TH}}}{Q} \cdot \left(q_{\text{max}} \cdot \left\{ m_0 - \left(m_0 \left(\frac{0.0532 \cdot V_{\text{eff}} + 1.10154}{100} \right) \right) \right\} - C_0 \cdot V_{\text{eff}} \right) \right]} \quad (12)$$

Where m_0 [g] is the initial weighed mass of adsorbent and m_{sorb} [mg] is the amount of analyte adsorbed on the solid.

3.2. Retention of Cs(I) on Circosil®

The retention of Cs(I) on Circosil® was investigated via MCE (with fraction collector) and via batch experiments. Fig. 3 shows the recovery (R) in [%] (BTC) and pH of MCE in 10 mM and 100 mM NaCl. Comparing the results for both eluents, a higher capacity of Cs(I) on Circosil® in 10 mM NaCl can be seen. This will be discussed in detail later. At this point it is also interesting to mention that here the same pH of 10.7 was reproducibly measured (analogue to the leaching study). As the measured Ca(II) and Si(IV) contents in the eluate are analogous to those in the leaching study, they are not listed and discussed again here.

Fig. 4 shows the Freundlich (Eq. (10)), Langmuir (Eq. (11)) and Thomas fits (Eq. (12)) of the data presented in Fig. 3. The Freundlich fits, with $R^2 = 0.939$ and 0.995 , represent the experimental data way better than the Langmuir ones ($R^2 = 0.814$ and 0.970). With that it can be said that the MCEs are more likely based on Freundlich kinetics. Thus, and the theoretical principles described in chapter 2.7, a reversible sorption of Cs(I) to Circosil® in a kind of multilayer at heterogeneous sorption sites (of different binding strength) is most likely at this point. This observation agrees very well with the literature, where one to three different adsorption sites (ion exchange, outer-sphere and inner-sphere complexes) are proposed [13,43–46]. But also, according to the literature, the main sorption process of Cs(I) on cement paste phases is ion exchange on the C-S-H phases [4,47–50].

On the other hand, even though the Thomas model is mathematical based on kinetics analogous to Langmuir, both lead to different results [35,39,40]. Comparison of the correlation coefficients shows that the Thomas model ($R^2 = 0.992$ and 0.991) reflects reality much better than the Langmuir isotherm and at some point, even better than the Freundlich isotherm. This circumstance makes sense in so far as the Thomas model (along with Yoon-Nelson and Bohart-Adams) is precisely

tailored to the fit of fixed-bed questions [51–54]. For this reason, the q_{max} values determined with the Thomas model are more reliable or reflect reality better than those calculated with the Langmuir isotherm. Another reason for the good Thomas fit could be due to the fact, that one dominant sorption process is assumed for the sorption of Cs(I) on C-S-H phases (see above). Thus, the kinetics is more like Freundlich, but has a noticeable Langmuir character due to the one dominant sorption process (homogeneous sorption sites). Nevertheless, the Thomas fits result in a q_{max} of 4.82 mg g^{-1} for Cs(I) on Circosil® in 10 mM NaCl and a q_{max} of

2.65 mg g^{-1} in 100 mM NaCl. Accordingly, a higher ionic strength of the electrolyte causes a drastic decrease of the Cs(I) capacity on C-S-H phases. A comparison of the Thomas constants ($0.27 \text{ mL mg}^{-1} \text{ min}^{-1}$ in 10 mM NaCl and $0.31 \text{ mL mg}^{-1} \text{ min}^{-1}$ in 100 mM NaCl) supports these observations, thus a higher K_{TH} underlies faster saturation. This result is also in a very good agreement with literature. There is described that the ionic strength of the electrolyte and the competing ions (Na^+ , K^+ , and Ca^{2+}) are the main factors influencing Cs(I) sorption on C-S-H phases [55,56]. It should be mentioned that the C/S ratio of the C-S-H phases also strongly determines Cs(I) sorption. Thus, a higher C/S causes a lower Cs(I) adsorption and vice versa [48,56]. In the presented experiments, C/S was always the same, so that the influence can be neglected.

The sorption behaviour of Cs(I) on Circosil® could be described very well by means of MCE. However, since this is a completely new approach for column experiments, it is recommended to compare the results with those of an established experiment: batch experiments. For this reason, Fig. 5 shows the R_d values from the MCE and the batch plotted against C_{eq} .

Fig. 5 shows that the MCEs provide a significantly higher amount of data compared to the batch experiments. From the MCE-data, physico-chemical parameters can be calculated more easily and, in case of doubt, more precisely. In the above case, the obtained data were fitted with simple exponential functions, the corresponding R_d values calculated for an C_{eq} of 15 mg/L Cs(I) and listed in Table 4. The value of C_{eq} was deliberately set to 15 mg/L since the column is saturated at this point and an equilibrium can be assumed.

The values in Table 4 show that the calculated $\log(R_d)$ values from MCE and batch are with a deviation of 2.0 % in 10 mM NaCl and 5.4 % in 100 mM NaCl close to each other. The influence of the ionic strength on the retention of Cs(I) on Circosil® can again be seen in both types of experiments. Since the Cs(I) sorption respectively the R_d values on C-S-H phases depend on the C/S ratio, the ionic strength of the electrolyte and also on the presence of competing ions, the values reported in the literature tend to vary greatly and a comparison is quite challenging [23,57]. A possible comparative value is provided by Missana et al. [56].

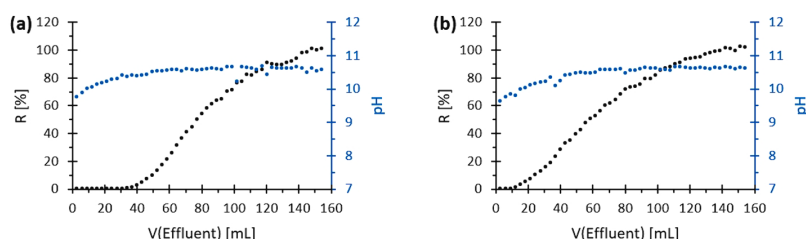


Fig. 3. Break through curve (BTC) of Cs(I) on Circosil® in [%] and pH plotted against the effluent volume for the MCEs: (a) in 10 mM (97.8 nmol Cs(I) per injection); (b) 100 mM NaCl (75.3 nmol Cs(I) per injection).

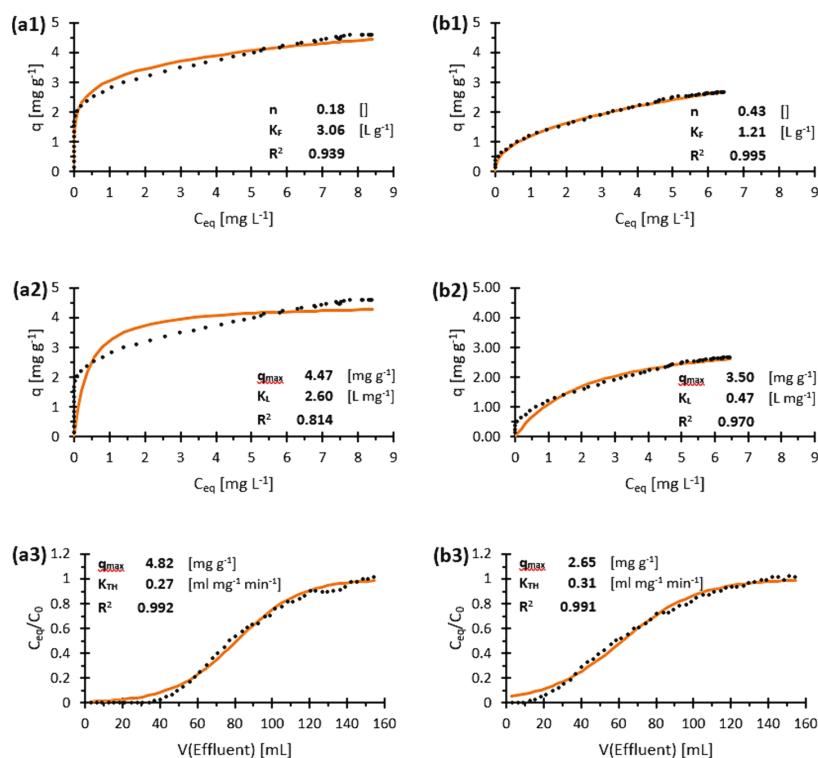


Fig. 4. Freundlich (1), Langmuir (2) and Thomas fit (3) for the MCEs with Cs(I) on Circosil® in 10 mM (a) and 100 mM NaCl (b).

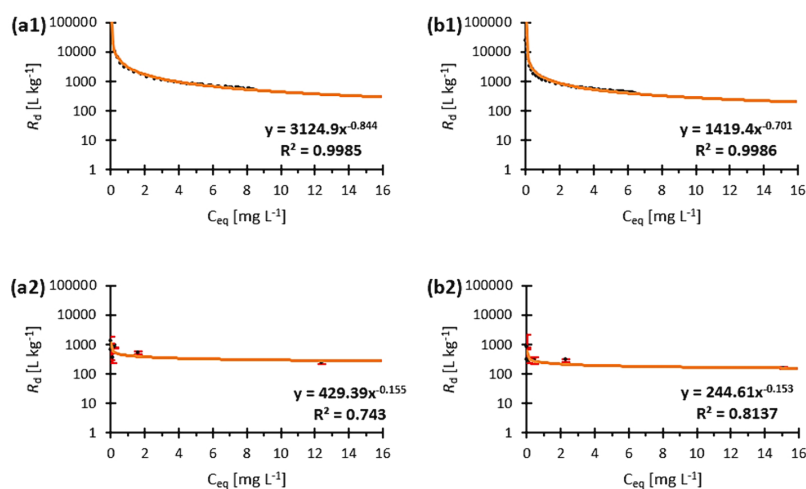


Fig. 5. R_d plotted against C_{eq} for Cs(I) in 10 mM NaCl (a) and 100 mM NaCl (b) obtained from MCE (1) and batch (2).

Table 4

Calculated R_d [L kg⁻¹] and $\log(R_d)$ values for miniaturised column experiments (MCE) and batch experiments.

$R_d/\log(R_d)$ [L kg ⁻¹]	Cs(I) on Circosil® in 10 mM NaCl	Cs(I) on Circosil® in 100 mM NaCl
MCE	318/2.50	213/2.33
Batch	282/2.45	162/2.21

They had found an R_d ($\log(R_d)$) of approximately 160 (2.20) L kg⁻¹ for Cs(I) with quite similar experimental conditions, which is in a very good alignment with the gained values.

Finally, it should be mentioned that MCEs have a duration of 4 to 5 days according to the method described in chapter 2.3. Whereas for a comparable batch experiment approx. 2 to 3 weeks must be planned. Thus, significantly more data points can be generated via the MCE in a shorter period of time. Furthermore, dynamic instead of stationary sorption parameters can be calculated from this. Due to the almost identical R_d values, this circumstance is of secondary importance here, but in case of doubt it can reflect reality way better. In addition, similar sorption distribution ratios from stationary and dynamic experiments are a good hint of fast sorption kinetics.

3.3. Retention of Eu(III) on kaolinite/sand (MCE with HPLC-ICP-MS coupling)

The leaching behaviour of the 3:7 wt% kaolinite/sand mixture was investigated in advance analogously to Circosil®. However, there was no pronounced leaching (max. 38.9 µmol/L Al(III) and max. 23.6 µmol/L Si(IV) in solution), so it will not be discussed in detail.

Two experiments were performed with HPLC-ICP-MS coupling as described in chapter 2.6 (1:9 wt% kaolinite/sand and 100 % sand) and one without coupling as described in chapter 2.3 (3:7 wt% kaolinite/sand). Previous studies by Kautenburger et al. (2022) and Sander (2017) presented a first rudimentary approach for MCE-HPLC-ICP-MS setup. As this was not a robust method but a first draft, it was not possible to determine sorption parameters of any kind [8,10]. Thus, the sorption capacity of the analyte only could have been estimated. Even with the method presented in this paper, instrumental quantification of C_{eq} in the eluate is only possible with great effort. Due to the chosen experimental setup, however, an elegant assumption can now be made: To determine the sorption parameters for Eu(III) on kaolinite/sand, the fact that $C_{eq} = C_0$ or $C_0/C_{eq} = 1$ applies to the eluate when the column is saturated can be utilised. Thus, it is necessary to ensure column saturation and to normalise the BTC to the highest signals measured. Fig. 6 shows the chromatogram from the measurement with Eu(III) (6.6 nmol per Injection) at 1:9 wt% kaolinite/sand, the resulting Thomas fit and how it is achieved. Because of the large amount of the raw data, the chromatograms were first averaged for each injection. The averaged signals where

Table 5

Fit Parameters for Eu(III) on different kaolinite/sand mixtures in 10 mM NaCl.

Ratio		Fit Parameters		
Kaolinite	Sand	q_{max} [mg g ⁻¹]	K_{TH} [mL mg ⁻¹ min ⁻¹]	R^2
0	10	0.09	224.7	0.996
1	9	0.12	63.9	0.997
3	7	0.22	1.43	0.983

than normalised to those of the internal standard (Ho) and fitted afterwards. Since the column was completely saturated, it is assumed for the fit, as described above, that the following applies for the largest normalised signal: $C_0/C_{eq} = 1$.

The dip in the chromatogram shown in Fig. 6 (1) is due to a small error in the measurement setup, which is well documented and did not distort the experiment in any way. Nevertheless, the affected data points are excluded for further consideration (see Fig. 6 (2) and (3)). Again, the Thomas model provides an excellent fit to the measured data with a $R^2 = 0.997$. This results in a q_{max} of 0.12 mg g⁻¹ and a Thomas constant of 63.9 mL mg⁻¹ min⁻¹ for Eu(III) at the 1:9 wt% kaolinite/sand mixture in 10 mM NaCl. The same procedure (shown in Fig. 6) was also applied to the measured data for Eu(III) on 100 % sand in 10 mM NaCl, whereas the data for Eu(III) on 3:7 wt% kaolinite/sand where evaluated as shown in Fig. 4 (since the experiment was performed analogously to the MCE with Cs(I) Circosil®). For a better comparison, the fit parameters for all Eu (III) experiments are listed in Table 5.

As can be seen from Table 5, a lower kaolinite content results in a lower q_{max} and a higher K_{TH} . Accordingly, the absorptive capacity of kaolinite towards Eu(III) must be significantly higher than that of sand. If the q_{max} values from Table 5 are now plotted against the kaolinite content used, it is possible to calculate the q_{max} for Eu(III) at 100 % kaolinite by linear extrapolation. The fit line of this linear regression is given as equation (13) ($R^2 = 0.988$).

$$q_{max} = 0.084 + 0.0044 \cdot (\text{fraction of kaolinite } [\%]) \quad (13)$$

With that a q_{max} of 0.52 mg g⁻¹ can be calculated for Eu(III) on kaolinite in 10 mM NaCl and the corresponding value for sand (0 % kaolinite) can be seen in Table 5 ($q_{max} = 0.09$ mg g⁻¹). As comparison, Kautenburger and Beck (2010) had found a q_{max} of 0.47 mg g⁻¹ for Eu(III) on kaolinite in 10 mM NaClO₄ using batch experiments at similar conditions [58].

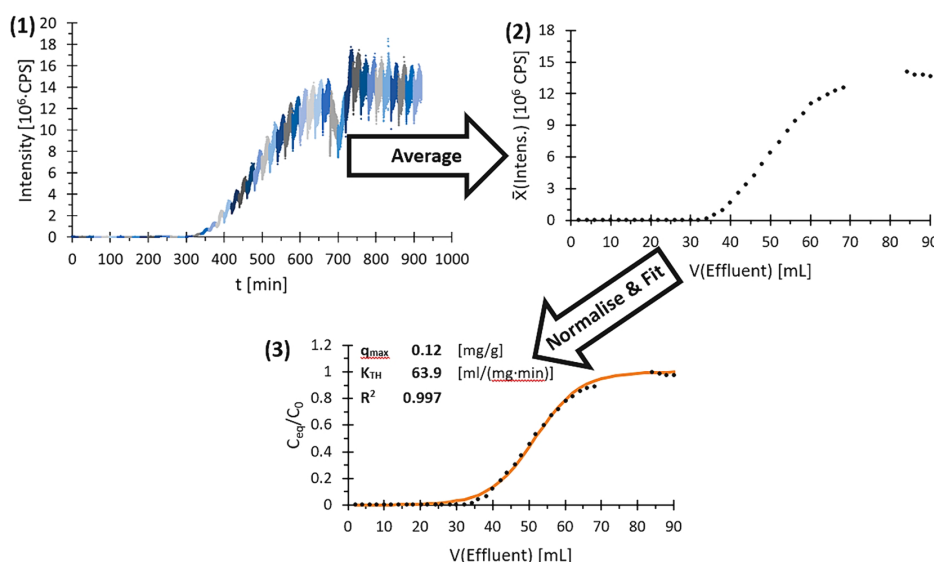


Fig. 6. Chromatogram (1) averaged signals for each injection (2) and resulting Thomas fit (3) for Eu(III) on 1:9 wt% kaolinite/sand in 10 mM NaCl.

Where on the other hand Qiu et al. (2019) had found an identical $q_{\max}$ of 0.09 mg g^{-1} for Eu(III) on sand [59]. The values for Eu(III) on sand fit excellently, while the ones obtained for Eu(III) on kaolinite deviates by 11 % from the literature. The reason for this small discrepancy can either be due to the normal uncertainty range or a slight overdetermination of $q_{\max}$ for Eu(III) on the 3:7 wt% kaolinite/sand mixture. The linear regression of the $q_{\max}$ values had shown that this one value is slightly above the fitted line. In addition, the coefficient of determination for this data point (0.983, cf. Table 5) is lower than that of the other two values, which could indicate a slight uncertainty of the value.

In the end it was proven that with HPLC-ICP-MS coupling MCEs can be carried out in just a few hours without additional treatment needed. With that the advantage of saving time defined at the end of chapter 3.2 weighs even more. However, there is also a small limitation here; due to the direct introduction of the eluate into the ICP-MS, the ionic strength of the eluate must be within the limits defined by the manufacturer. Consequently, coupling using Circosil® as adsorbent is not possible. But for most sorbents, the direct coupling method and data evaluation presented here can be used to determine realistic sorption data very fast.

4. Conclusion

In this study, a new method for fast and dynamic sorption experiments using HPLC, ICP-MS and HPLC-ICP-MS coupling, including a new approach for data evaluation, is presented.

With the MCE-method a maximum loading capacity of 4.82 mg g^{-1} in 10 mM NaCl and 2.65 mg g^{-1} in 100 mM NaCl was determined for Cs(I) on Circosil®. Maximum loading capacities are also achievable by batch but only with greater effort and not with this reliability. Therefore, for a MCE-batch-comparison, the obtained $\log(R_d)$ values were compared. With $\log(R_d)$ of 2.50/2.45 L kg^{-1} (MCE/batch) in 10 mM NaCl and 2.33/2.21 L kg^{-1} in 100 mM NaCl, those differed only by 2.0 % and 5.4 % and where also in a good alignment with literature. Accordingly, it was shown that MCEs can not only be used to determine more sorption parameters, but also much faster and, due to the significantly higher data density, more accurately than with a conventional batch method.

Apart from sorption experiments, another possible application for MCE was presented. In the context of C-S-H phases, the same experimental setup was used to perform a leaching study on Circosil®. A reproducible leaching behaviour of Circosil® was demonstrated, which again is in excellent agreement with the literature. From this, a simple model for predicting the mass loss of Circosil® in the column as a function of the eluent volume could be derived.

In addition, the MCE method has been further developed to implement an even faster online quantification via direct HPLC-ICP-MS coupling. Thus, a maximum loading capacity of 0.52 mg g^{-1} was determined for Eu(III) on kaolinite in 10 mM NaCl and 0.09 mg g^{-1} on sand. Those results are again in a very good alignment with the literature.

In summary, this study presented a new experimental method (including data evaluation) for performing fast and dynamic sorption and leaching experiments by means of MCEs. Dynamic retention coefficients and maximum loading capacities for two different analytes on several adsorbent materials could be determined easily and very accurately. The method presented works much faster, with less resources and more controllable than the conventional experimental setups. In this context, controllable means, that the pressure, temperature, flow and gradient of the eluent can be precisely monitored and adjusted. In addition, the MCE method should also be easily applicable to a wider range of analytes and adsorbent materials; something that will be investigated in the future.

CRedit authorship contribution statement

Aaron Haben: Writing – original draft, Visualization, Validation,

Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kristina Brix:** Writing – review & editing, Validation. **Nico Bachmann:** Visualization, Investigation. **Ralf Kautenburger:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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3.1.3 Behaviour of Mo(VI), Eu(III) and U(VI) in Calcium-Silicate-Hydrate Phases: Immobilisation and Dynamic Remobilisation under Repository-Relevant Conditions

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Table 5: Author contribution roles for the publication "Behaviour of Mo(VI), Eu(III) and U(VI) in Calcium-Silicate-Hydrate Phases: Immobilisation and Dynamic Remobilisation under Repository-Relevant Conditions" in form of the CRediT standard [8].

Contributor roles	Author(s)
Conceptualisation	Aaron Haben, Ralf Kautenburger
Methodology	Aaron Haben, Nico Bachmann
Validation	Aaron Haben, Nico Bachmann, Jan Jakob Langer, Ralf Kautenburger
Formal analysis	Aaron Haben, Nico Bachmann
Investigation	Aaron Haben, Nico Bachmann
Writing – original draft	Aaron Haben, Jan Jakob Langer
Writing – review and editing	Aaron Haben, Nico Bachmann, Jan Jakob Langer, Ralf Kautenburger
Visualisation	Aaron Haben, Nico Bachmann
Data curation	Aaron Haben, Nico Bachmann
Supervision	Ralf Kautenburger
Project administration	Ralf Kautenburger
Funding acquisition	Ralf Kautenburger

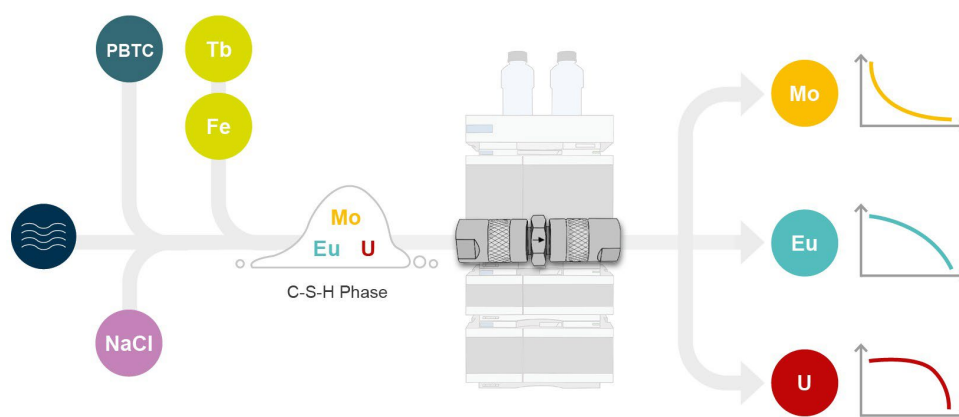


Figure 22: Graphical abstract to the publication "Behaviour of Mo(VI), Eu(III) and U(VI) in Calcium-Silicate-Hydrate Phases: Immobilisation and Dynamic Remobilisation under Repository-Relevant Conditions" [8].

Extended abstract:

Since C-S-H phases are essential for the safety assessment of the geotechnical barrier system in HLW repositories and to ensure its long-term safety, it is important to know how and to what extent radionuclides are retained by the C-S-H phases. To date, there have been numerous and extensive studies on the retention of repository-relevant elements in C-S-H phases, but little to no data on the remobilisation dynamics of such elements, and even less under realistic conditions (dynamic and suitable S/L ratio). Furthermore, in batch experiments, only limited information under rather unrealistic conditions is gained. The MCEs, on the other hand, promise a far more realistic and therefore more suitable approach to conducting leaching experiments.

In this study, C-S-H phases were incorporated with Mo(VI), Eu(III) and U(VI) during the synthesis. For this purpose, the analytes were added to the reaction solution at concentrations of $5 \cdot 10^{-5} \text{ mol L}^{-1}$ and $5 \cdot 10^{-4} \text{ mol L}^{-1}$ (S/L = 50 g L^{-1}). The aim was to investigate the (dynamic) remobilisation behaviour of the analytes in the C-S-H phases under conditions representative for a German HLW repository. For this purpose, the influence of the ionic strength, that of a cement additive (PBTC) and the influence of two potential competition ions (Fe(III) and Tb(III)) were investigated.

Elemental analysis of the supernatant solutions, using ICP-QQQ, confirmed the successful incorporation of all three elements into the C-S-H phases. In all cases, quantitative retention was observed for Eu(III) and U(VI), while Mo(VI) was only retained/incorporated by about 50%. X-ray diffractometry showed that the synthesis was successful and no effects of the added elements on the structure of the C-S-H phases could be recognised. Both with and without the incorporated analytes, a disordered $11 \text{ \AA}$ tobermorite structure is assumed. Furthermore, the ICP-QQQ analysis revealed that the synthesised C-S-H phases had a C/S ratio of 1.066 ± 0.003 and thus an excellent reproducibility of the synthesis was proven.

The leaching behaviour of the incorporated C-S-H phases was first investigated with ultrapure water in standardised batch experiments and MCE. The results obtained confirmed the expected leaching behaviour for Si(IV) and Ca(II). In the case of Eu(III) and U(VI), little to no remobilisation and thus

quantitative retention was observed in both, batch and MCE. These observations are consistent with data from batch experiments in literature. However, the literature does not provide a clear picture of the remobilisation of Mo(VI), which was here remobilised after only a few pore water exchange cycles, although not completely. The remobilisation curve indicates two different retention mechanisms: a weakly bound adsorption on/in the C-S-H structure and precipitation of CaMoO_4 . These mechanisms had been suspected before, but this is the first time they have been substantiated.

Furthermore, the data collected from both, batch and MCE, showed clear differences. The leaching/remobilisation of all elements was significantly stronger pronounced in the batch setup, which was contributed to the different equilibrium states of the pore water cycles and the different S/L ratios. Since MCEs are more representative for the repository-relevant conditions, all further experiments to investigate the effects of the repository-relevant parameters were conducted using only MCEs.

Increasing the ionic strength up to 1 M increased the leaching of Ca(II) and Si(IV), whereas an increase to $I = 2$ M resulted in a decrease in leaching for both elements. Here the formation of silicate agglomerates is assumed, to which Ca(II) can adsorb again. However, this presumed mechanism must be confirmed by future investigations. An increased ionic strength (up to $I = 2$ M) had no significant influence on the remobilisation of Eu(III) and Mo(IV), but for U(VI). In contrast to some literature reports, a slight but significant increase in U(VI) remobilisation at $I = 2$ M was proven here. The cause is assumed to be the cleavage of a Ca(II)-mediated U(VI) retention mechanism. Since the pore waters in a potential North German repository are expected to be highly saline, additional investigations with high ionic strength electrolytes are therefore recommended.

The addition of the competitive ions Fe(III) and Tb(III) as displacement agents had no influence on the remobilisation dynamics of Eu(III) and U(VI). Any displacement effects are therefore unlikely. However, an increase in the leaching of Si(IV) and Ca(II) was observed. A substitution of the SiO_4 tetrahedra and the bridging Ca^{2+} ions in the C-S-H phase structure is suspected. More importantly, the addition of the competition ions delayed the remobilisation of Mo(VI), what indicated the precipitation of insoluble trivalent metal molybdates.

PBTC as a potential cement additive and complexing agent increases the leaching of Si(IV), Ca(II), Eu(III) and U(VI), whereas that of Mo(VI) is slightly delayed. PTBC has a considerable effect on the C-S-H phases, where, besides the complexation of cations, several other interaction mechanisms are involved. For example, a proposed precipitated calcium phosphonate layer on the C-S-H surface leads to a delayed but rapid remobilisation of U(VI). In Addition, Eu(III) was faster remobilised compared to U(VI), indicating a preferential complexation of Eu(III). In the case of the delayed Mo(VI) remobilisation, co-precipitation of molybdenum calcium phosphonates is postulated. However, to make definitive statements about the postulated mechanisms, further investigations are necessary.

To summarise, this comprehensive study provides important dynamic data on the retention and remobilisation dynamics of Mo(VI), Eu(III) and U(VI) under representative repository conditions. This has closed important gaps in the literature and provided new and very interesting insights for repository research.



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Behaviour of Mo(VI), Eu(III) and U(VI) in calcium-silicate-hydrate phases: Immobilisation and dynamic remobilisation under repository-relevant conditions

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ABSTRACT

Calcium-silicate-hydrate (C-S-H) phases play an essential role as a geotechnical barrier in high-level nuclear waste (HLW) repositories. To guarantee the long-term safety of a HLW disposal site, it is important to know how and to which degree radionuclides are retained by C-S-H phases. To this date, only little to no data on the remobilisation dynamics of the repository-relevant elements Mo(VI), Eu(III) and U(VI) under realistic conditions are available. In this study, C-S-H phases incorporating these elements were synthesised, the element immobilisation was quantified via ICP-QQQ and their structure was investigated via X-ray diffractometry. All C-S-H phases had a calcium-silicon ratio (C/S) of 1.066 ± 0.003 and no relevant structural influences of the studied elements could be observed. In all cases, quantitative immobilisation was observed for Eu(III) and U(VI), whereas Mo(VI) was retained/incorporated to only about 50 %. Afterwards, their leaching behaviour with ultrapure water was studied in batch and mini-column experiments (MCE). Mo(VI) was remobilised quickly, while Eu(III) and U(VI) were retained nearly quantitatively. Due to the more realistic and therefore more representative conditions, further experiments to investigate the effects of three repository-relevant parameters were conducted only using MCE. A higher ionic strength significantly enhanced U(VI) remobilisation, while Eu(III) and Mo(VI) remained nearly unaffected. The displacement agents Fe(III) and Tb(III) only affected Mo(VI)'s remobilisation by retarding it. The addition of a complexing agent (2-phosphonobutane-1,2,4-tricarboxylic acid; PBTC) led to a delayed remobilisation of Mo(VI), while Eu(III) and U(VI) were remobilised to some degree after sufficient PBTC elution. Overall, this work delivers important information on key processes relevant to nuclear waste disposal.

1. Introduction

With the discovery of radioactivity, numerous new technologies emerged to harness radioactive processes but also brought the challenge of disposing the resulting high-level nuclear waste (HLW). This mainly involves spent fuel elements from nuclear power plants, waste from the reprocessing of these and material from decommissioned nuclear weapons (Oelkers and Montel, 2008). To effectively protect future generations from the harmful effects of radionuclides and their fission products, the final storage of HLW in deep geological formations is envisaged (Kautenburger and Beck, 2008; Freiesleben, 2013; Jobmann et al., 2017; Lommerzheim et al., 2019). Cement-based materials are a crucial component in such future HLW, but also in intermediate (ILW) and low-level waste (LLW) repositories. Due to their physical and chemical stability and their ability to immobilise hazardous substances,

they are used as construction or sealing materials (Atkins et al., 1992; Evans, 2008; Ochs et al., 2016; Luhr et al., 2023). Therefore, understanding the retention behaviour of repository-relevant elements under geochemical conditions on cement phases is of great interest.

In contact with penetrating pore water hydrated cement is not thermodynamically stable. This results in cement aging phases, which consist essentially of calcium silicate hydrate (C-S-H) phases. Since the majority of both freshly hydrated and aged cement consists of C-S-H phases and they are considered to be responsible for the heavy metal binding ability of cementitious materials, they are crucial for the safety assessment in repository research (Spence, 1993; Gaona et al., 2011; Ochs et al., 2016; Baur et al., 2022). In contact with aqueous media C-S-H Phases degrade, whereby the molar calcium to silicon (C/S) ratio decreases within approx. 36,000 years from 1.5 to 0.8 due to the leaching of Ca(II) (Jacques et al., 2009; Baston et al., 2012). The

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resulting pore water has an alkaline pH of about 12.5, which decreases with decreasing C/S ratio to approximately 10. The alteration of the C–S–H phases is very complex, particularly due to their semi-crystalline structural characteristics and the involved dissolution and precipitation reactions (Baston et al., 2012; Lothenbach and Nonat, 2015; Papatzani et al., 2015; Ochs et al., 2016). C–S–H phases synthesised by co-precipitation are predominantly described as a semi-crystalline cement gel with either a 11 Å or 14 Å tobermorite structure (Richardson, 2008; Baston et al., 2012; Papatzani et al., 2015; Kee et al., 2021). Thereby structural models by Grangeon et al. (2016) suggest that an increasing Ca(II) content leads to enhanced Ca^{2+} intercalation within the tobermorite interlayers and, at even higher C/S ratios, to the formation of $\text{Ca}(\text{OH})_2$ both and outside the C–S–H structure. Despite these complexities, C–S–H phases remain the principal sorbing component of cementitious barriers throughout repository evolution.

Radionuclides originating from the near field of the disposal site can be adsorbed or even incorporated into the C–S–H structure of the surrounding geotechnical barriers (Ochs et al., 2016). Among these, uranium, as one of the main components of spent nuclear fuel, is of particular interest (Motta et al., 2015; Brix et al., 2023). In C–S–H phases it is primarily present in the oxidation state + VI (Harfouche et al., 2006; Macé et al., 2013; Wolter et al., 2019). Many studies have observed high U(VI) retention via surface complexation, incorporation into the C–S–H structure, precipitation, or the formation of ternary Ca(II)–U(VI) surface species/phases (Evans, 2008; Tits et al., 2008, 2011, 2015; Baqer et al., 2023; Macé et al., 2023). Androniuk et al., for example, identified mono- and bidentate outer-sphere complexes of UO_2^{2+} with the deprotonated oxygen atoms of the bridging Si(IV)-tetrahedra. Thereby, due to the sorption of Ca^{2+} ions on the same sorption sites, a competition between UO_2^{2+} and Ca^{2+} has been suggested (Androniuk et al., 2017; Androniuk and Kalinichev, 2020). Despite the formation of negatively charged aqueous U(VI) species at pH > 10, the U(VI) retention by C–S–H gel increases with increasing C/S ratio, suggesting a U(VI) uptake mechanism involving Ca^{2+} from the C–S–H interlayers (Pointeau et al., 2004; Wolter et al., 2019; Macé et al., 2023).

Europium is an important radionuclide in the context of nuclear decommissioning (Efremenkov and Drape, 2007) and is often used as a less toxic and non-radioactive homologue for the trivalent actinides Cm(III) and Am(III) (Eisenbud et al., 1984; Krauskopf, 1986; Tits et al., 2003). Pointeau et al. (2001) have shown that Eu(III) is nearly quantitatively immobilised by C–S–H, mainly by substitution of Ca^{2+} in the C–S–H structure, and by near-surface complexation or precipitation. In this context, it was shown that no precipitation of Eu(III) hydroxide was observed and thus sorption to C–S–H dominated the retention mechanism, while a higher C/S leads to a stronger binding of Eu(III). These results thus reflect the rest of the literature; with one important exception: in other publications, in a pH range >10, precipitation is indeed reported as part of the retention (Tits et al., 2003; Mandaliev et al., 2011; Kee et al., 2021; Baur et al., 2022; Burešová et al., 2023; Dettmann et al., 2023). Furthermore, Kee et al. (2021) have shown that the incorporation of Eu(III) during C–S–H synthesis significantly inhibits crystal growth and reduces particle size.

For molybdenum, only limited retention on C–S–H phases is reported. Ochs et al. (2016) (and sources within) and Lange et al. (2020) reported a measurable contribution of C–S–H phases to the total retention of Mo(VI) in Portland cement, with increased retention at higher C/S ratios. This is attributed to electrostatic adsorption on a positively charged C–S–H surface ($\text{C/S} \geq 1.2$) and is therefore associated with a strong pH influence: OH^- and MoO_4^{2-} can compete for those sorption sites. In structural studies, Caselles et al. (2021) were unable to detect any changes in the C–S–H structure due to incorporated Mo(VI). However, they identified the precipitation of powellite (CaMoO_4) as the main retention mechanism. It can therefore be assumed that the increasing Mo(VI) retention with a higher C/S is due to a larger number of electrostatic sorption sites as well as a higher Ca(II) concentration and thus a favoured powellite precipitation. Notably, Grambow et al. (2020)

negatively highlighted substantial inter-laboratory variability in Mo(VI) retention data, underlining the need for further studies.

Despite the extensive body of literature on retention mechanisms (mainly for Eu(III) and U(VI)), data on the remobilisation or leaching of radionuclides from C–S–H phases remain scarce. For Mo(VI) and Eu(III) remobilisation or leaching, no valid literature data is available, while the existing data for U(VI) are limited and insufficiently representative regarding the conditions for potential repositories. The influence of repository-relevant factors (e.g. ionic strength, competition/displacement ions or cement additives) has not been sufficiently investigated. Moreover, previous investigations exclusively relied on static batch experiments, which can only approximate conditions expected in a repository environment. Dynamic column experiments provide a more realistic representation of radionuclide transport and leaching behaviour but are often resource-intensive and therefore rarely applied. Haben et al. (2024) have recently presented a remedy in the form of mini-column experiments (MCE). This approach enables systematic investigation of remobilisation processes under controlled flow conditions while minimising experimental effort.

The present work is intended to address all the described gaps in knowledge by investigating the retention, structural effects, and dynamic remobilisation of radionuclides from C–S–H phases under repository relevant conditions. Therefore, C–S–H phases with incorporated Mo(VI), Eu(III) and U(VI) were synthesised, both as single elements and as a mixture, in two different concentrations. After quantifying the retention and analysing the structural effects, the radionuclide remobilisation was investigated. Therefore, standardised batch and dynamic MCE were conducted in ultrapure water. Subsequently, the influence of the ionic strength of the electrolyte (up to 2 M NaCl; depending on disposal side up to 5 M are conceivable; Brix et al. (2021) and sources within), the influence of the cement additive PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid) as potential complexing agent (Rickert and Thielen, 2004; Kretzschmar et al., 2022) and the potential displacement by Fe(III) and Tb(III) were investigated. In many countries (including Germany), the HLW container is to be made of a steel alloy, what inevitably leads to corrosion of the alloy and thus to large amounts of Fe(III) ions in the vicinity of the repository (Féron et al., 2008; Burger et al., 2013; Dörr et al., 2013; Shrestha et al., 2021; Feng et al., 2024). Regarding Tb(III): Due to the chemically similar behaviour of the trivalent lanthanides (*Ln*) and actinides (*An*), it is common practice in nuclear science to investigate the behaviour of *Ln* as a stable substitute for *An* (Cross et al., 2016; Ochs et al., 2016; Welch et al., 2017). Because of the high similarities the *Ln* group (Cotton, 2006; Hege et al., 2024) Tb(III) is therefore particularly interesting as a displacement ion for Eu(III).

Based on the dynamic experimental approaches, this study provides new mechanistic insights into radionuclide remobilisation from C–S–H phases and demonstrates the practicality of MCE as an efficient tool for repository research.

2. Materials and methods

2.1. Chemicals

Ultrapure water ($0.055 \mu\text{S cm}^{-1}$) (PURELAB® Chorus 1 ultrapure water filtration unit, Elga LabWater, High Wycombe, UK) was used to prepare all solutions. NaCl with premium-grade quality (EMSURE®) from Merck (Darmstadt, Germany) was used to prepare the eluents for MCEs and the electrolytes for the batch experiments. HNO_3 (Rotipuran® Supra 69 %, Carl Roth, Karlsruhe, Germany) was used to acidify the measurement solutions, whereas HCl (30 % Suprapur®, Merck Supelco®, Darmstadt, Germany) and NaOH (Suprapur® 30 %, Merck, Darmstadt, Germany) were used to adjust the pH in the experiments. For the displacement and leaching experiments Fe(III) (1 g L^{-1} in 2–3 % HNO_3 , Merck Certipur®, Darmstadt, Germany) and Tb(III) (10 g L^{-1} in 2 % HNO_3 , AccuStandard, New Haven, USA) inductively coupled

plasma mass spectrometry (ICP-MS) standard solutions and a 50 wt% PBTC solution (2-Phosphonobutane-1,2,4-tricarboxylic Acid, TCI, Tokyo, Japan) were used. A solution with 10 mg L⁻¹ of Sc(III) (1 g L⁻¹ in 5 % HNO₃, Alfa®, Karlsruhe, Germany), Y(III) (1 g L⁻¹ in 2–3 % HNO₃, Merck Certipur®, Darmstadt, Germany) and Ho(III) (1 g L⁻¹ in 2–3 % HNO₃, Merck Certipur®, Darmstadt, Germany) in 5 % HNO₃ was prepared as the internal standard stock solution for all inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ) measurements. Argon 5.0 (Ar ≥ 99.999 mol%, ALPHAGAZ™ 1 Argon, Air Liquide, Düsseldorf, Germany) was used as plasma gas for ICP-QQQ measurements. For the experiments and ICP-QQQ calibration, Mo(VI) (1 g L⁻¹ in 1 mol L⁻¹ with traces HF, Bernd Kraft, Duisburg, Germany), Eu(III) (10 g L⁻¹ in diluted HNO₃, Agilent, Kingstown, USA) and U(VI) (1 g L⁻¹ in 2–5 % HNO₃, AccuStandard, New Haven, USA) ICP-MS standard solutions were used. Furthermore, Ca(II) (1 g L⁻¹ in 0.5 mol L⁻¹ HNO₃, Merck Certipur®, Darmstadt, Germany) and Si(IV) (10 g L⁻¹ in water, Tr. HF, AccuStandard, New Haven, USA) standards were used for ICP-QQQ calibration of the leaching experiments.

2.2. Synthesis of the C–S–H phases

The most common synthesis route for C–S–H phases is the co-precipitation from an aqueous solution/suspension with CaO and SiO₂ as precursors (Atkins et al., 1992; Tits et al., 2006; Gaona et al., 2011; Wolter et al., 2019; Kee et al., 2021). According to Grangeon et al. (2016), it can be assumed that, starting from a pure tobermorite structure (at C/S = 0.67), an increase of the C/S ratio leads to increased Ca²⁺ intercalation into the tobermorite interlayer and ultimately to the precipitation of Ca(OH)₂. At a C/S < 1.5, Ca(OH)₂ still forms within the tobermorite structure, while at C/S > 1.5 it also forms outside the crystal structure. Since the focus of this work is on the different of “external” conditions relevant to a repository and not on the effects of varying C/S ratios, a decision had to be made on one C/S ratio. Taking the above into account, a C/S between 0.67 and 1.5 is advisable. Therefore, a C/S of 1.07 was chosen here (CaO to SiO₂ mass ratio of 1).

For the synthesis of the C–S–H phases, CaO (≥99.95 %, metals basis, Thermo Scientific, Darmstadt, Germany) and SiO₂ (Aerosil® 300, SiO₂ ≥99.8 %, BET 270–330 m² g⁻¹, Evonik Operations, Essen, Germany) were mixed with ultra-pure water in 50 mL centrifuge tubes (Ultra-High Performance Centrifuge Tubes, PP, 20000g, VWR, Randor, USA) with a solid to liquid ratio (S/L) of 50 g L⁻¹ and a C/S of 1.07. The reaction mixture was shaken in a rotary shaker (Stuart®, Rotator SB3, Cole-Parmer®, Vernon Hills, USA) at 40 rounds per minute for 4 weeks under Ar atmosphere (Ar ≥ 99.999 mol%, ALPHAGAZ™ 1 Argon, Air Liquide, Düsseldorf, Germany). They were then centrifuged for 30 min at 16990g (centrifuge 3-18 KS, Sigma, Osterode am Harz, Germany), the supernatant was decanted under Ar atmosphere and stored for further investigation. The solid phases were then dried under vacuum in a desiccator over silica gel until the weight remained constant.

For the incorporated C–S–H phases, Mo(VI), Eu(III) or U(VI) were added solo (“Mo-y”, “Eu-y”, “U-y”) or as a mixture (Waste Cocktail; “WC-y”) to the reaction mixture. The analyte solutions were pH-neutralised in advance. In all cases, two different concentrations for each analyte in the reaction mixture was chosen: 5•10⁻⁵ mol L⁻¹ (“x-L”) and 5•10⁻⁴ mol L⁻¹ (“x-H”). An additional batch was subsequently prepared for the WC sample in the lower concentration (“WC-L-2”), as the initial quantity was not sufficient. The concentrations of the analytes in the “WC-L-2” reaction solution deviate slightly: for Mo(VI) the concentration was 4.64•10⁻⁵ mol L⁻¹, for Eu(III) 5.49•10⁻⁵ mol L⁻¹ and for U(VI) it was 5.13•10⁻⁵ mol L⁻¹. Based on a quantitative retention, the added analyte contents result in a maximal possible analyte concentration of 1•10⁻⁶ mol g⁻¹ in the “x-L” C–S–H phases (slightly different for “WC-L-2”) or 1•10⁻⁵ mol g⁻¹ in the “x-H” ones.

To determine the exact analyte contents in the respective C–S–H phases, an indirect quantification during and after the synthesis was performed. All used and accumulated supernatant solutions and reaction

tubes were analysed towards the corresponding analytes. ICP-QQQ quantification was performed as described in Chapter 2.6.

2.3. XRD measurement

Powder X-ray diffraction (PXRD) patterns of the different samples were recorded at room temperature on a D8-A25-Advance diffractometer (Bruker, Karlsruhe, Germany) in case of air-stable samples, while air-sensitive samples were measured on a X'Pert MPD diffractometer (PANalytical, Almelo, Netherlands) using dome sample holders. In both cases, measurements were performed in Bragg-Brentano θ - θ -geometry (goniometer radius D8 280 mm; MPD 240 mm) with Cu K α -radiation (λ_1 = 154.0596, λ_2 = 154.4426 p.m.), as well as a 12 μ m Ni foil working as K β filter and a variable divergence slit at the primary beam side. A LYNXEYE detector with 192 channels was used at the secondary beam side on the D8-A25-Advance and a PIXcel^{1D} detector on the X'Pert MPD diffractometer. Experiments were carried out in a 2θ range of 7–120° with a step size of 0.013° and a total scan time of 2 h.

2.4. Mini column experiments (MCE)

The column experiments carried out are based on the recently published MCE method by Haben et al. (2024). This method allows the execution of extremely resource- and time efficient leaching experiments. The mini columns used are HPLC guard columns (UPC-130B, UPCHURCH SCIENTIFIC™, Oak Harbor, USA), drilled out to 3.5 mm inner diameter, with a 500 nm pore size filter disc (A-103X, UPCHURCH SCIENTIFIC™, Oak Harbor, USA). The dry C–S–H phases were filled into the column with a suitable funnel and thereby gradually compacted. The HPLC components used are Agilent 1100, 1200 and 1260 Infinity II HPLC systems (Waldbronn, Germany) and are listed in Table 1.

The MCE were performed with ultrapure water, 0.1 M, 1 M and 2 M NaCl as eluent with a column temperature of 25 °C. The columns were packed with approx. 147 mg of C–S–H (exact weight was considered in the respective experiments) and then preconditioned in the HPLC for 150 min using a flow gradient from 10 to 40 μ L min⁻¹. The eluate of the preconditioning step was also collected. After preconditioning, the flowrate of the eluent was set to 40 μ L min⁻¹. In total, an MCE experiment lasts 65 h (including preconditioning) with a total pore volume of 154 mL, and for MCE in presence of PBTC, a total of 127.5 h with a total pore volume of 304 mL. Depending on the experiment, 10 μ L of either a 1.7•10⁻⁴ mol L⁻¹ Fe(III), 1.4•10⁻⁴ mol L⁻¹ Tb(III) or 63.6•10⁻³ mol L⁻¹ PBTC solution were injected multiple times into ultrapure water (eluent) via the autosampler. For Fe(III)-displacement a 100-fold equivalent (over 100 injections), for Tb(III)-displacement also a 100-fold equivalent (over 100 injections) and for the PBTC-leaching a total of 1000-fold equivalent (over 200 injections) were injected; all equivalences are in relation to the amount of Eu(III) on the column. After the column, the entire eluate was collected by means of a fraction collector. Samples were taken from the individual fractions for an ICP-QQQ measurement,

Table 1
Components and software of used HPLC system for MCE.

Hardware:	
1100 Series G1379A Degasser	1260 Infinity II G7111B Quaternary Pump
1100 Series G1312A Binary Pump	1260 Infinity II G7129A Vialsampler
1100 Series G1313A Autosampler	1260 Infinity II G7116A Multicolumn Thermostat
1100 Series G1316A Column oven	1260 Infinity II G7117C Diode Array Detector
1100 Series G1315B Diode Array Detector	1200 Series G1364C Fraction collector
1200 Series G1364C Fraction collector	
Software:	
ChemStation for LC 3D Systems Rev. B.02.01-SR2 [260]	OpenLab CDS ChemStation Edition Rev. C.01.10 [322]

and the pH values were determined (pH-meter SevenMulti, pH-electrode InLab®, Mettler Toledo, Columbus, USA). ICP-QQQ quantification was performed as described in Chapter 2.6.

2.5. Batch experiments

The batch experiments were conducted for additional validation of the still new dynamic MCE method. All leaching experiments in ultrapure water were therefore performed as batch and MCE.

All the batch experiments were prepared in triplicates, where 10 mL of ultrapure water was added to 40.0 ± 0.2 mg of the respective C–S–H phase ($S/L = 4 \text{ g L}^{-1}$) in a 15 mL polypropylene (PP) centrifuge tube (Ultra-High Performance Centrifuge Tube, VWR® International, Darmstadt, Germany), followed by equilibration in a horizontal shaker (Pro-max 1020 platform shaker, Heidolph Instruments, Schwabach, Germany) at room temperature. Every 24 h the pH was measured, 5 mL of sample was taken and subsequently refilled with 5 mL fresh ultrapure water. This was repeated until a total pore water (exchange-) volume of 75 mL was reached. On weekends, the 24-h rhythm could not be maintained, so that the batch experiments extended over a total period of 21 days. ICP-QQQ quantification was performed as described in Chapter 2.6.

2.6. ICP-QQQ measurements

For the ICP-QQQ measurement, an Agilent 8900 ICP-QQQ (Santa Clara, USA) with an Agilent SPS 4 autosampler (Santa Clara, USA) was used. The measurements were performed with the parameters given in Table 2 and with different cell gas modes: ^{28}Si and ^{40}Ca were measured in H_2 -reaction gas mode via mass pair (Q_1, Q_2) = (28, 28) and (Q_1, Q_2) = (40, 40). ^{95}Mo , ^{153}Eu , ^{157}Tb and ^{238}U were measured in “NoGas”-mode and ^{56}Fe in He collision gas mode. For quantification, an external calibration was performed.

3. Results and discussion

3.1. Amounts of analytes bound/immobilised to C–S–H

The respective analyte contents of the solid phases can be derived from analysing the elemental contents of the reaction tube walls and the supernatant solutions after C–S–H phase synthesis. These are shown in Table 3. If the resulting C/S is calculated from the values listed there, the average value is 1.066 ± 0.003 . Based on the synthesis route described in Chapter 2.2, a C/S of 1.07 would have been expected. Thus, the reproducibility of the C–S–H phase synthesis is excellent.

Based on the absolute amounts added during synthesis and the quantities found in the supernatant and on the tube walls, the proportion bound to/in the C–S–H phases can be calculated for each analyte. The absolute quantities in the fractions “bound,” “supernatant,” and “tube walls” are listed in the supplementary information in Table S1, and the relative proportions are shown in Fig. S1. For a better overview, only the actual bound/incorporated amounts of substance (R [%]) are shown in Fig. 1. It shows that retention/incorporation values of ≥ 99.94 % were determined for Si(IV), >98.7 % for Ca(II), between 46.9 % and 59.3 % for Mo(VI), >97.8 % for Eu(III), and >98.9 % for U(VI). Table S1 and

Table 3

Si(IV), Ca(II), Mo(VI), Eu(III) and U(VI) concentrations (c) in all synthesised C–S–H phases, derived from analyte content in supernatant solution and on reaction tube walls after the C–S–H phase synthesis; Single element phases: “Mo-y”, “Eu-y” and “U-y”; Multi element phases: “WC-y”; in low (“x-L”) and high (“x-H”) concentration; initial concentrations see Chapter 2.2.

C–S–H Phase	c(Si) [mmol g ⁻¹]	c(Ca) [mmol g ⁻¹]	c(Mo) [μmol g ⁻¹]	c(Eu) [μmol g ⁻¹]	c(U) [μmol g ⁻¹]
U-L	7.566	8.067	–	–	0.905
U-H	7.459	7.934	–	–	8.867
Mo-L	7.582	8.098	0.538	–	–
Mo-H	7.439	7.929	4.829	–	–
Eu-L	7.556	8.073	–	0.888	–
Eu-H	7.582	8.091	–	9.057	–
WC-L_1	7.652	8.164	0.515	0.918	0.919
WC-L_2	7.500	8.002	0.478	0.986	0.921
WC-H	7.652	8.101	4.289	9.187	9.158

Fig. S1 also show where the missing, unbound fractions of the respective analytes are located. In the case of Mo(VI), this was found almost exclusively in the supernatant solution, so that non-incorporation can be assumed; the same applies to Ca(II). In the case of Eu(III) and U(VI), however, a large part of the non-incorporated amount was measured on the tube walls, and in the case of Si(IV), the unbound fraction is divided almost equally between the supernatant and the tube walls. Overall, however, an almost quantitative retention (incorporation) can be assumed for the elements Si(IV), Ca(II), Eu(III), and U(VI). It is also worth mentioning that almost identical R [%] were determined for “WC-L_1” and “WC-L_2”, once again underlining the excellent reproducibility of the C–S–H synthesis.

As mentioned in the introduction, the retention and incorporation of Eu(III) and U(VI) on/in C–S–H phases is well described in literature, whereas the one for Mo(VI) is only insufficiently described. The literature reports almost quantitative retention for U(VI), caused by precipitation, intercalation into the interlayers, direct surface complexation and the formation of ternary Ca(II)-uranate-like surface precipitates (see Introduction). Similarly, quantitative retention on C–S–H phases is reported for Eu(III), which is mainly immobilised by incorporation into the C–S–H structure (Ca^{2+} substitution) and surface complexation/precipitation. At pH values < 10 , sorption dominates, with a higher C/S increasing the binding, whereas at pH values > 10 , precipitation is also observed as a retention mechanism (see Introduction). For example, Brix et al. (2023) reported for a distribution ratio (R_d) of approx. 10,000 L kg^{-1} for Eu(III) and approx. 20,000 L kg^{-1} for U(VI) (at $S/L = 4 \text{ g L}^{-1}$ and $C/S = 0.83$). To give a better comparison, these literature R_d values must be converted into R [%]. Equation (1) shows how R_d [L kg^{-1}] values are calculated, where V [L] is the volume of the electrolyte, m [kg] the mass of the adsorbent, n_{eq} [mol] the analyte amount in solution and n_{sorb} [mol] the amount of analyte adsorbed/retained. Based on equation (2), the corresponding retention values R [%] can be calculated from the R_d values listed in the literature. In the case of Brix et al. (2023) this results in a quantitative retention for Eu(III) and U(VI), of 98 % and 99 %. When putting the data listed in Table S1 and Fig. 1 (Fig. S1) in context to the literature, there is very good agreement.

$$R_d = \frac{n_{\text{sorb}}}{n_{\text{eq}}} \frac{V}{m} \quad (1)$$

$$R = \frac{R_d}{\frac{V}{m} + R_d} \cdot 100\% \quad (2)$$

The assessment of Mo(VI) is somewhat more difficult. There is not only few, but also widely differing retention and incorporation data available. In general, Mo(VI) shows only limited and low retention on C–S–H phases, where a higher C/S leads to an increasing retention. The

Table 2

Parameters of all ICP-QQQ measurements.

RF Power	1550 W
Plasma gas flow rate	15.0 L min^{-1}
Nebuliser gas flow rate	1.03 L min^{-1}
Integration time	300 ms
Sweeps per replicate	20
Dwell time	15 ms
Replicates	3
H_2/He gas flow	$4.8 \cdot 10^{-3}/4.1 \cdot 10^{-3} \text{ L min}^{-1}$

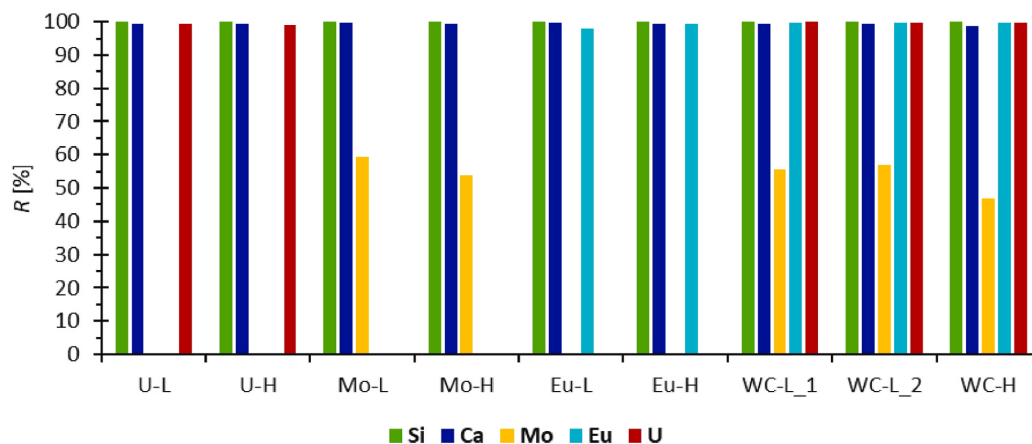


Fig. 1. Percentage retention values (R [%]; relative amounts incorporated and/or bound) of Si(IV), Ca(II), Mo(VI), Eu(III) and U(VI) in/on the synthesised C-S-H phases (values from Fig. S1); nomenclature see Table 3.

increased retention at higher C/S ratios ($C/S \geq 1.2$) is probably due to the higher number of electrostatic sorption sites and the higher Ca^{2+} concentration, which favours powellite precipitation ($CaMoO_4$) (see Introduction). For example, Lange et al. (2020) report R_d values of approx. 430 L kg^{-1} with an S/L of 40 g L^{-1} and a C/S of 0.9. However, the retention mechanism is not clearly explained, although adsorption is suspected. Grambow et al. (2020) refer, in part, to the data described by Lange et al. (2020) and define an R_d range of $4\text{--}430 \text{ L kg}^{-1}$ ($C/S = 0.8\text{--}0.9$). Caselles et al. (2021) can be used as a further reference, with reservations. Here, an R_d of approx. 1000 L kg^{-1} was determined at a C/S of 1.6, but this time the precipitation of $CaMoO_4$ is considered the main retention mechanism. In view of the significantly higher C/S, this result also fits very well into the picture. Converting those data using equation (2), this results in a Mo(VI) retention on C-S-H of approx. 6%–95% at a S/L of 5 g L^{-1} to 40 g L^{-1} and a C/S of 0.8–1.6. Thus, it can be stated that the retention mechanism of Mo(VI) on C-S-H phases as well as its quantification is only insufficiently described. Literature therefore does not provide an adequate comparison, and the values determined here must be considered in isolation for the time being. The underlying mechanisms are explained in more detail in Chapter 3.3.

3.2. Structural analysis

If the structure of C-S-H phases needs to be assigned, this is not always easy due to the semi-crystalline properties. Fig. 2 shows the diffractograms of a C-S-H phase without (“C-S-H”) and a one with the incorporated elements (“WC-H”). Even without a detailed data analysis/refinement, a classification of the solid phases is possible. The structure of C-S-H phases and thus corresponding XRD data are reported in several publications. Both solid phases show the typical, literature-known reflexes (*) (Caselles et al., 2021; Kee et al., 2021; Baur et al., 2022). Furthermore, no differences were observable between the solid phases investigated. Based on the work of Grangeon et al. (2013), the reflexes at $2\theta \approx 17^\circ$, 29° , 32° and 50° can be considered as an evidence for a $11 \text{ \AA}$ tobermorite structure; more specifically a disordered $11 \text{ \AA}$ tobermorite structure. According to Kee et al. (2021), it is the reflex at $2\theta \approx 7^\circ$, that allows the clear identification as $11 \text{ \AA}$ tobermorite. However, it should also be mentioned that the tobermorite structure can only be expected in the C-S-H synthesis route chosen here (co-precipitation). In a hydrothermal process, for example, a xonotlite structure is reported (Kee et al., 2021).

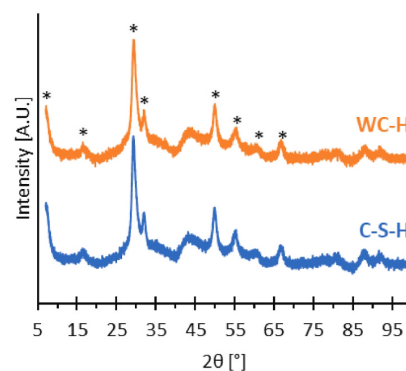


Fig. 2. X-ray diffractograms of the C-S-H phases without (“C-S-H”) and with incorporated analytes (“WC-H” sample; see Table 3).

3.3. Remobilisation in ultrapure water

The remobilisation of the analytes from the synthesised C-S-H phases in ultrapure water will now be discussed. For this purpose, the remaining amounts in [%] of Mo(VI), Eu(III) and U(VI) in the “WC-H” solid phase (relative to the initial values listed in Table 3) derived from batch and MCE experiments are shown in Fig. 3. The presentation of Si(IV) and Ca(II) is deliberately omitted in Fig. 3, as it would be detract

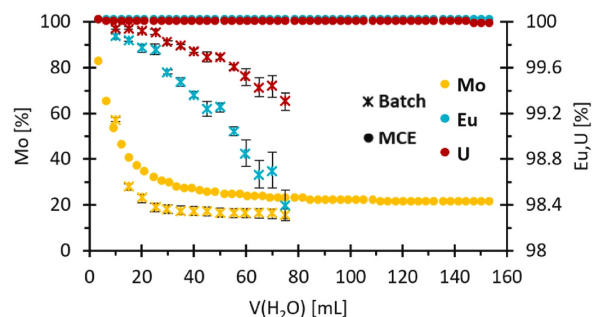


Fig. 3. Remaining Mo(VI), Eu(III) and U(VI) [%] in “WC-H” sample (see Table 3) plotted against pore water volume during batch- and MCE-leaching experiments.

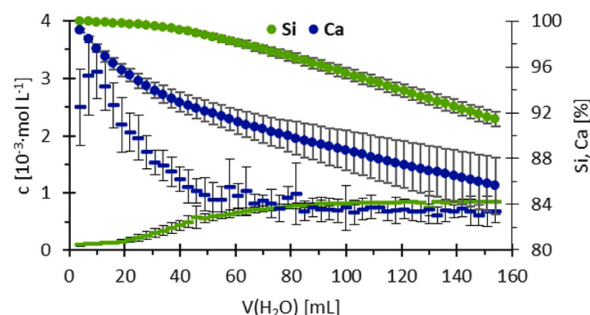


Fig. 4. Leached Si(IV) and Ca(II) concentrations (bars) as well as remaining Si(IV) and Ca(II) amounts in [%] (dots) averaged over all MCE experiments plotted against the eluent volume (H_2O).

from clarity and will be discussed in more detail in Fig. 4. Additionally, the leached amounts [%] of all analytes in all experiments with ultrapure water are listed in Table 4.

Looking at Fig. 3, it is immediately apparent that all analytes in the “WC-H” sample leach significantly more in the batch experiments compared to the MCE setup. The same is true for all the other leaching experiments in ultrapure water (see Table 4). This fact becomes more striking in view of the used pore water/elution volume; less was used in the batch experiments (75 mL) compared to MCE (154 mL). Two reasons can be assumed for this: Firstly, depending on the experimental set-up, different “chemical equilibria” can be assumed. While the batch experiments are static systems, where each leaching step equilibrates for at least one day (in total 21 d), the MCE setup can be considered as dynamic; the eluent flows through the column continuously (in total 65 h). Therefore, the longer equilibration time in the batch, could be considered as one reason for the differences in the leaching behaviour. Another possible reason could be the different S/L of the two experimental conditions. While the pore water in the MCE can only occupy the space/pores in the solid phase and can therefore be regarded as natural or realistic, the S/L in batch experiments can only be regarded as an approximation. In the batch setup, there is way more electrolyte available for equilibrium than in the MCE setup. The consideration of equation (1) can mathematically substantiate this hypothesis: If a reasonably constant R_d value for the retention on C–S–H phases is assumed in both experimental setups, a higher electrolyte volume (V) results in a lower value for n_{soib} (and vice versa results in a higher value for n_{eq}). To further substantiate the influence of the S/L, the work of Wang et al. (2009) can be used. By investigating sorption behaviour of caesium on granite (in batch experiments) and by comparing their results with those from Li et al. (2009) (using columns), they reported that the S/L ratio was probably the decisive factor in the different results

obtained from batch and column experiments. Thus, the combination of longer equilibration times and lower S/L leads to a stronger pronounced remobilisation in the batch setup.

Regarding U(VI), in all experiments extremely low remobilisation was observed (both batch and MCE) (see Table 4). Thus, in connection with H_2O , one can speak of a nearly quantitative retention. Although no literature data on dynamic remobilisation studies could be found, the results are in excellent agreement with those of retention/adsorption studies. Quantitative retention of U(VI) on C–S–H phases is generally reported, with remobilisation only increasing due the formation of soluble carbonate species (Wolter et al., 2019; Maragkou and Pashalidis, 2022; Schmeide et al., 2025). However, as already mentioned, there is a difference in the leaching behaviour when comparing batch experiments and MCE, especially in the “x-H” samples. For example, in the “WC-H” sample (see Fig. 3 and Table 4) 0.7 % of the original U(VI) amount was leached in the batch, whereas only 0.02 % was leached in the MCE. The reason that this difference in U(VI) leaching is more pronounced in the “x-H” samples can be explained by the involvement of different retention mechanisms. Those with significantly higher R_d values could dominate in the “x-L” samples, so that a change in the S/L has a less significant effect.

In the MCE setup, a marginally lower remobilisation can be determined for Eu(III) compared to U(VI) (see Fig. 3 and Table 4). Conversely, Eu(III) leaching is significantly increased in the batch experiments. The same assumption can be made here as above for U(VI), with the difference, that in the case of Eu(III) the effect of a higher electrolyte volume is clearly noticeable in both, the “x-L” and “x-H” samples. No literature data on leaching from C–S–H phases are available for Eu(III), Am(III) or Cm(III). However, to create a literature comparison, the publication by Goo et al. (2021) can be used. They investigated Eu(III) leaching from Portland cement and reported very little to almost no Eu(III) remobilisation.

As already mentioned, significantly stronger pronounced leaching of Mo(VI) can be observed in the batch experiments compared to the MCE. The reasons are analogous to the other analytes. Much more interesting at this point is the kinetic of the Mo(VI) leaching itself. At the beginning, Mo(VI) is remobilised very quickly and to a large extent, whereas towards the end it is leached very slowly. This observation suggests that at least two different retention/remobilisation mechanisms are involved. Based on the curve shown, a comparatively weak adsorption and either strong incorporation or precipitation is obvious. If the solubility product of powellite (CaMoO_4) is considered, precipitation can be assumed as the most likely process. During the synthesis, $4.46 \cdot 10^{-1} \text{ mol L}^{-1} \text{ CaO}$ and either 50 or $500 \cdot 10^{-6} \text{ mol L}^{-1} \text{ MoO}_4^{2-}$ are used (see Chapter 2.2). Based on the pK_{sp} value of 7.72 ($K_{\text{sp}} = 1.91 \cdot 10^{-8} \text{ mol}^2 \text{ L}^{-2}$) reported by Essington (1990), CaMoO_4 precipitation can therefore be expected. Even with the Ca(II) and Mo(VI) concentrations in solution at the beginning of the leaching experiments itself, this solubility product is still exceeded. For example, in the MCE experiment described in Fig. 3, $3.99 \cdot 10^{-3} \text{ mol L}^{-1} \text{ Ca(II)}$ (see Fig. 4) and $3.07 \cdot 10^{-5} \text{ mol L}^{-1} \text{ Mo(VI)}$ (see supplementary data Fig. S2) were measured in the first fraction (product = $1.22 \cdot 10^{-7} \text{ mol}^2 \text{ L}^{-2}$). This observation is also confirmed by Caselles et al. (2021). There, co-precipitation as CaMoO_4 is postulated as the main retention mechanism, although the possibility of surface adsorption could not be ruled out. However, no proof was provided. Here, on the other hand, the remobilisation kinetics visible in Fig. 3 can be regarded as strong indication for a combination of weak surface adsorption and the precipitation of CaMoO_4 .

Apart from the differences between batch and MCE, the leaching behaviour of Si(IV) and Ca(II) agrees with literature data. In summary, it can be said that C–S–H phases with a C/S < 0.83 initially leach more Si(IV), whereas C–S–H phases with a C/S > 0.83 initially leach more Ca(II). If a C/S = 0.83 is reached in both cases, the C–S–H phases dissolve congruently (Si(IV) and Ca(II) leach to the same extent) (Baston et al., 2012; Walker et al., 2016). Based on the C/S of 1.066 ± 0.003 averaged from Table 3, increased Ca(II) leaching would be expected at

Table 4
Amounts of remobilised analytes in [%] (in relation to the values listed in Table 3) at the end of the leaching single element (SE) and multi element (WC) experiments in ultrapure water; C–S–H with low (L) and high (H) analyte concentration; amount of pore water in batch setup = 75 mL and in MCE setup = 154 mL.

			Amounts leached [%]				
			Mo	Eu	U	Si	Ca
Batch	SE	L	75.5	1.34	0.35	11.1	16.8
		H	83.5	1.00	0.60	10.9	17.3
	WC	L	76.1	2.22	0.62	11.4	16.5
MCE	SE	H	84.0	1.61	0.70	9.9	17.8
		L	72.3	0.11	0.42	8.6	13.3
	WC	H	74.6	<0.01	0.02	8.6	14.6
		L	72.9	0.02	0.08	8.5	17.1
		H	79.8	<0.01	0.02	7.1	14.2

the beginning. Fig. 4 shows both, the concentrations and the remaining quantities of Si(IV) and Ca(II) plotted against the elution volume; both averaged over all MCEs with ultrapure water. In fact, a high Ca(II) concentration (over $3 \cdot 10^{-3} \text{ mol L}^{-1}$) was measured in the first fractions, which decreases up to a pore volume of 80 mL (approx. $7 \cdot 10^{-4} \text{ mol L}^{-1}$). The reverse is true for Si(IV). The measured Si(IV) concentration increases up to a pore volume of 80 mL: from initially below $1 \cdot 10^{-4}$ to approx. $8 \cdot 10^{-4} \text{ mol L}^{-1}$. Since the measured Si(IV) and Ca(II) concentrations can be regarded as constant from an H₂O volume of 80 mL, congruent leaching can also be assumed here. However, it should also be mentioned that the Ca(II) leaching was significantly less reproducible and more error-prone than that for Si(IV) (see Fig. 4). As discussed above, Ca(II) is suspected to be more involved in the retention mechanisms of the other analytes and is therefore also subject to greater fluctuations due to different analyte leaching and possible re-immobilisation (such as co-precipitation after leaching).

There were no significant differences in the measured pH values. In the batch, an average pH of 11.3 ± 0.1 was determined at the beginning of the experiments and a pH of 10.84 ± 0.07 at the end. In the MCE, the average pH was 11.73 ± 0.09 at the beginning and 10.78 ± 0.07 at the end of the experiments (same can be seen for MCEs described below; supplementary Figures S3, S5 and S8). The marginally higher initial pH in the MCE can again be explained by the significantly higher S/L ratio. The reason for the decrease in pH values over the duration of the experiments lies in the Ca(II)-leaching. Since all C-S-H phases leach significantly more Ca(II) (compared to Si(IV)), it can be assumed that the C/S decreases over the course of the experiment and thus the pH of the pore water also decreases (see Introduction).

3.4. Remobilisation in dependence of ionic strength

Based on the results and interpretations from Chapter 3.3, it was concluded that the implementation of MCE leaching experiments reflects natural conditions better than batch experiments. For this reason, no batch experiments were conducted when investigating the effects of different ionic strengths; the same applies for all later sections.

Fig. 5 shows the leaching curves of Mo(VI), Eu(III) and U(VI) from the incorporated “WC-L₁” C-S-H phase for different ionic strengths (0–2 M NaCl). For better comparability, the resulting leached quantities are listed in Table 5.

Neither for Mo(VI) nor for Eu(III) any significant influence of the ionic strength on the leaching behaviour can be observed. A comparison of the values for ultrapure water and those for different ionic strengths shows no differences (within the limits of the fluctuation ranges). From Table 4, an averaged leaching of $75 \% \pm 3 \%$ can be determined for Mo(VI) over all MCE in ultrapure water; for Eu(III) $0.03 \% \pm 0.05 \%$. Compared with the values from Table 5, an averaged value of $75 \% \pm 3 \%$ results for Mo(VI) and $0.02 \% \pm 0.00 \%$ for Eu(III) in different ionic

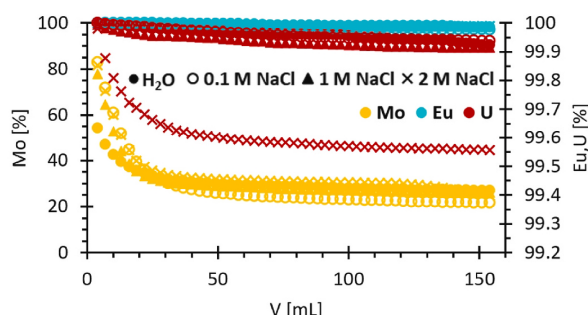


Fig. 5. Remaining Mo(VI), Eu(III) and U(VI) [%] in “WC-L₁” sample (see Table 3) plotted against pore water volume in different ionic strength solutions; all were conducted as MCE-leaching experiments.

Table 5

Amounts of remobilised analytes in [%] from “WC-L₁” (in relation to the values listed in Table 3) at the end of MCE leaching experiments with different ionic strength (data from Fig. 5 and S4); each after 154 mL elution volume.

Eluent	Leached amount [%]				
	Si	Ca	Mo	Eu	U
H ₂ O	8.5	17.1	72.9	0.02	0.08
0.1 M NaCl	14.9	24.9	78.4	0.02	0.06
1 M NaCl	25.3	33.7	73.7	0.01	0.09
2 M NaCl	12.5	28.9	75.1	0.01	0.44

strengths. In view of the results for Si(IV) and Ca(II) leaching (see next paragraph), a Ca(II)-mediated sorption on or in the C-S-H structure thus seems rather unlikely for Mo(VI) and Eu(III).

The Si(IV) and Ca(II) leaching curves (analogous to Fig. 5), the measured Si(IV) and Ca(II) concentrations and the measured pH are listed in the supplementary data (Fig. S3 and S4). Fig. S3 also shows that the ionic strength does not influence the pH in any way. For Si(IV), the total leached amount increases from 8.5 % in ultrapure water to 25.3 % in 1 M NaCl; in the case of Ca(II) from 17.1 % to 33.7 % (see Table 5 and Fig. S4). Subsequently, in the step from 1 M to 2 M NaCl, the leached amount decreases again: for Si(IV) to 12.5 % and for Ca(II) to 28.9 %. The increased Ca(II) leaching with higher NaCl concentration is in excellent agreement with the literature. Wolter et al. (2019) conducted batch experiments and have measured a similar tendency for Si(IV) and Ca(II) as a function of ionic strength but unfortunately failed to provide any explanation. Glasser et al. (2005) have shown that the Ca(II) solubility increases significantly up to an ionic strength of 1.5 M NaCl. The increase in Ca(II) solubility is mainly attributed to the formation of calcium chlorido complexes. Hill et al. (2006) and Sugiyama (2008) also report an increased Ca(II) release with increased ionic strength. In contrast, they postulated a cation exchange of Ca^{2+} by Na^+ as the decisive mechanism.

The leaching behaviour of Si(IV) and Ca(II) at ionic strengths above 1.5 M NaCl is barely reported in the literature. In particular, the decrease in leaching behaviour between 1 M and 2 M NaCl observed by us has not been described previously. Our results show a clear decrease in leaching between 1 M and 2 M NaCl, which contradicts the few available literature data on Si(IV) solubility. Glasser et al. (2005) found hardly any influence of increasing NaCl concentrations (up to 1.46 M) on Si(IV) solubility, more so, they report that at low C/S (0.85) the Si(IV) solubility should be slightly reduced by increasing aqueous NaCl concentrations. This observation is in clear contradiction to the values in Fig. S4/Table 5 and Fig. S3. Due to the insufficient data and lack of specific experiments at this ionic strength, there are various potential explanations for this phenomenon. The most plausible would be that Ca^{2+} is not only substituted in the interlayer, but also at SiO_4^{4-} tetrahedron-bridging sites. This would partially break up the C-S-H structure, resulting in increased Si(IV) leaching; in form of silicate mono-, oligo- and polymers. This idea would result in silicate agglomerates forming and precipitating from a certain threshold value of monomers, oligomers or polymers. Accordingly, this threshold value of silicate species in the eluate would be reached between 1 M NaCl and 2 M NaCl. If silicate agglomerates were to form in addition to the C-S-H phases in the saline solution, this would create new sorption sites for cations such as Ca^{2+} . This would also explain the slight decrease in Ca(II) leaching from 1 M to 2 M NaCl.

In the case of U(VI), Table 5 and Fig. 5 show an influence only at an ionic strength of 2 M NaCl. Thus, from 1 M to 2 M NaCl, the amount leached increases in by a factor of 5. With that, a relatively large increase is visible, whereas in absolute terms one can still speak of near quantitative retention. These results contradict the ones of Wolter et al. (2019). They reported that an increased ionic strength leads to increased Ca(II) leaching and with that affects the structural integrity of C-S-H phases but has no to negligible effect on U(VI) remobilisation from those.

However, they did also mention a higher Si(IV) concentration (compared to Ca(II)) at a C/S = 0.99 after 768 h leaching with water (S/L = 1.2 g L⁻¹), which fundamentally contradicts not only this work (see Fig. 4 and Fig. S3), but also all findings from the literature (see above). A better agreement is achieved with Schmeide et al. (2025). There, the release of U(VI) due to an increase in ionic strength is considered minimal. Due to the experimental setup (batch with only one pore water cycle), they could not make any further statement regarding the retention/remobilisation mechanisms involved. Here, with the combination of the initially rapid and then again slow leaching behaviour of U(VI) in 2 M NaCl, it can be concluded that only one retention mechanism should strongly depend on the ionic strength of the electrolyte. Based on the equally strong influence on Ca(II) remobilisation, a Ca(II)-mediated U(VI) remobilisation would be obvious here. As already described in the introduction, Ca²⁺-mediated retention mechanisms are well known in the case of C-S-H phases. Furthermore, Brix et al. (2021) described analogous Ca²⁺ bridges that contribute significantly to the retention of UO₂(OH)₃⁻ or UO₂(OH)₄²⁻ on Ca-bentonite. The fact that only relatively small amounts of U(VI) (compared to Ca(II)) are remobilised here is probably because the Ca²⁺-mediated retention mechanism is strong but only develops to a very small extent (compared to the total retention of U(VI)). Therefore, this small proportion of bound U(VI) is only remobilised at the highest ionic strength. Together with the conclusions drawn above, coordination of UO₂(OH)₃⁻ or UO₂(OH)₄²⁻ to SiO₄ tetrahedron-bridging Ca²⁺ would therefore be conceivable. The decrease in Ca(II) leaching from 1 M NaCl to 2 M NaCl seems to contradict this working hypothesis, but as already mentioned above, it can be assumed that Ca(II) gets partially re-immobilised on formed silicate agglomerates.

Due to the experimental setup and the reproducibility shown in the experiments, combined with the agreement with the literature (in some cases), it was shown that the remobilisation of U(VI) from C-S-H phases depends (to a small extent) on the ionic strength of the electrolyte. Moreso, a possible Ca(II)-mediated retention/remobilisation mechanism dependent on ionic strength can be assumed, although this hypothesis urgently needs to be substantiated by further experiments.

3.5. Influence of Fe and Tb on leaching behaviour

To assess the influence of Fe(III) and Tb(III) as potential displacement agents, the respective leaching curves of Mo(VI), Eu(III) and U(VI) of the incorporated “WC-L2” C-S-H phase are plotted in Fig. 6. Analogous to Chapter 3.4, the leached quantities at the end of the respective MCEs are listed in Table 6. In addition, it should also be mentioned that for Fe(III) and Tb(III) a quantitative retention of 99.9 % and >99.9 % on

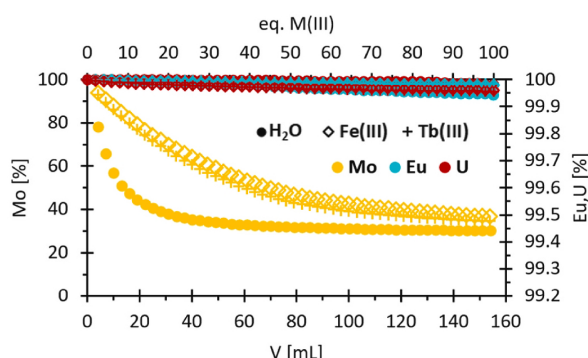


Fig. 6. Remaining Mo(VI), Eu(III) and U(VI) [%] in “WC-L2” sample (see Table 3) plotted against pore water volume during MCE leaching experiment with and without injected displacement agent M(III) (M = Fe, Tb; equivalents in relation to incorporated Eu(III)).

Table 6

Amounts of remobilised analytes in [%] from “WC-L2” (in relation to the values listed in Table 3) at the end of MCE leaching experiments with and without injection of different displacement agents (data from Fig. 6, S6 and S7); each after 154 mL elution volume.

Displacement agent	Leached amount [%]				
	Si	Ca	Mo	Eu	U
H ₂ O	9.3	14.9	69.9	0.06	0.02
Fe(III)	19.0	27.0	63.3	0.02	0.04
Tb(III)	17.2	29.1	65.3	0.02	0.04

the “WC-L2” C-S-H phase was observed.

When comparing Tables 4 and 6 (resp. Figs. 3 and 6), no significant influence of Fe(III) or Tb(III) on the leaching behaviour of Eu(III) and U(VI) can be observed; unlike for Si(IV), Ca(II) and Mo(VI).

So far, there is no literature data for comparable displacement experiments available. Nevertheless, to create at least some basis for argumentation, the work of Schmeide et al. (2025) is used again. There, the influence of Al(III) in C-A-S-H (calcium aluminosilicate hydrate) phases on their structure and their U(VI) retention properties was systematically investigated. When Al(III) is added in the C-S-H synthesis, AlO₄-tetrahedra can form bridging positions of the silicate chains. This leads to an increase in the average chain length and creates additional sorption sites for U(VI). The increasing amount of AlO₄-tetrahedra in the bridging positions of the silicate chains in turn leads to a decrease in the C/S and an increase in the interlayer distance. In a similar study, Pardal et al. (2009) reported that Al(III) is incorporated very rapidly into the C(A)-S-H structure, mainly by substitution of Si(IV), but also by insertion at the surface or in the interlayer of the C(A)-S-H phases. However, also calcium carboaluminate and/or strätlingite secondary phases can be detected as soon as a Ca²⁺ concentration of >4 mmol L⁻¹ was reached.

Mancini et al. (2020) published a comprehensive study on Fe(III) retention in C-S-H phases. In it, they report an extremely high retention of Fe(III) regardless of the C/S ratio and the pH of the background electrolyte. There, *R_d* (*K_d*) values of approx. 700,000 L kg⁻¹ were obtained (at 5 g L⁻¹). This results in retention values of 99.97 % (according to Equation (2)), which is consistent with the results obtained here. More importantly Mancini et al. (2020) concluded from the different effects of the pH and the Ca(II) concentration, that Fe(III) in C-S-H must have a different binding mechanism, compared to Al(III). From the pH independence, they conclude that the primary Fe(III) retention mechanism is probably not based on surface complexation, and since the C/S ratio is also irrelevant, it must be the C-S-H structure per se, so that an Al(III) analogous substitution of tetrahedrally coordinated Si(IV) at the bridge position is inconceivable. Regarding the binding mechanism, it is postulated that Fe(III) coordinates octahedrally directly to the Si tetrahedra in the interlayer of the C-S-H phases at a C/S ratio between 1.2 and 1.5. At lower C/S ratios, coordination in the interlayer is rather excluded and the formation of a separate secondary Ca-Si-rich Fe(III) phase (or cluster) on the surface of C-S-H is proposed. Based on the C-S-H phases used in this work (C/S = 1.066 ± 0.003), both the formation of Ca- and Si-rich Fe(III) secondary phases and octahedral coordination in the interlayers are conceivable.

In the context of an adsorbed/incorporated lanthanide Kee et al. (2021) and Pointeau et al. (2001) have shown that Eu(III) substitutes Ca²⁺ on the cation sites. Since there are no literature references available for Tb(III) and trivalent cations share several chemical similarities, some parallels between Al(III), Fe(III), Eu(III) and Tb(III) have to be drawn here (for the time being).

Analogue to Chapter 3.4, the Si(IV) and Ca(II) leaching curves, the measured Si(IV) and Ca(II) concentrations and the measured pH are listed in the supplementary information (Figs. S5 and S6). Looking at those, as well as Table 6, a clear influence of Fe(III) and Tb(III) on the leaching behaviour of Si(IV) and Ca(II) can be observed. Especially in

Fig. S5 a significantly increased Si(IV) and Ca(II) leaching is shown when Fe(III) or Tb(III) are involved. These observations partly contradict those of Schmeide et al. (2025), who only reported a significantly increased Ca(II) concentration in solution when Al(III) is involved. The reason for this could be the different experimental setups. While they had equilibration times of >67 d at room temperature, a dynamic system (MCE) was used here. Compared to dynamic experiments, a batch only represents the beginning of a leaching curve. This means that all literature data from batch experiments are comparable with the first approx. 10 mL of the leaching curves. This results in an enormous loss of information when conducting batch experiments, and the results appear contradictory. It inevitably follows, that the data presented here must be considered more representative, and thus proving the influence of displacement agents on both Si(IV)- and Ca(II) leaching.

Based on the literature described above, the increased Si(IV) and Ca(II) release can be interpreted in a way that Fe(III) and Tb(III), similar to Al(III) and Eu(III), replace Si(IV) or Ca(II) in the C-S-H structure. In the case of Fe(III), the retention mechanism on C-S-H phases is very well described by Mancini et al. (2020) (see above). They further propose a possible substitution of Ca(II) in the interlayer by Fe(III), depending on the C/S ratio (1.2 and 1.5). Given the electron configuration and the ionic radius, for Tb(III), similar to Fe(III), an octahedral coordination is also plausible, as shown by Ananias et al. (2001) (Tb(III) in silicate solid phases). Furthermore, as already mentioned, Pointeau et al. (2001) have shown for Eu(III) and Mancini et al. (2020) for Fe(III) that Ca(II) substitution in the C-S-H phase structure have to be considered. In principle, this mechanism would also be conceivable for Tb(III). An indication for this is the decreasing C/S with increasing Al(III) content shown by literature (Schmeide et al., 2025). Assuming that SiO₄-bridging Ca²⁺ ions are also leached/substituted in the process, the amount of leached Si(IV) would increase. Based on the literature and the data presented here, this substitution mechanism appears to be the most likely cause of the increased Si(IV) and Ca(II) leaching.

In addition, a clear influence of Fe(III) and Tb(III) is also visible for Mo(VI) remobilisation. Compared to ultrapure water, the leaching is significantly delayed, whereas in the end almost the same amounts were remobilised (see Fig. 6 and Table 6). In view of the higher Ca(II) concentration, a powellite precipitation is rather unlikely, since no similar phenomena was observable with an increased ionic strength electrolyte (e.g. 1 M NaCl). At this point, a Fe(III)- and Tb(III)-MoO₄ precipitate could be possible. Based on the solubility product of Fe₂(MoO₄)₃•7H₂O ($K_{SP} = 3.16 \cdot 10^{-28} \text{ mol}^5 \text{ L}^{-5}$), a possible precipitation can be estimated (Wedepohl, 1974). Considering the Eu(III) concentration listed in Table 3 and that 139.7 mg of the “WC-L2” C-S-H phase was packed into the column, a total amount of 137.7 nmol Eu(III) can be concluded. For a 100-fold excess, 13.77 μmol Fe(III) is required, which corresponds to an Fe(III) concentration of $8.94 \cdot 10^{-5} \text{ mol L}^{-1}$ (for an elution volume of 154 mL). This results in a solubility limit for Mo(VI) of $3.41 \cdot 10^{-7} \text{ mol L}^{-1}$. In both experiments, with Fe(III) and Tb(III), a Mo(VI) concentration of approx. $1.1 \cdot 10^{-6} \text{ mol L}^{-1}$ was measured in the first fraction (supplementary data Fig. S7). This decreased rapidly and fell below the solubility limit after an elution volume of approx. 60 mL. Accordingly, precipitation with molybdate can therefore be expected; at least for Fe(III). For Tb(III) there is unfortunately no literature data regarding the solubility product, but rare earth-/lanthanide-molybdates are often used as phosphors, optical fibres, scintillators, laser hosts and are therefore well-known to literature (Brixner et al., 1979; Huang et al., 1989; Pourmortazavi et al., 2019). One possible synthesis route is the direct precipitation reaction in an aqueous environment, as described, for example, by Pourmortazavi et al. (2019). This can be associated with a low solubility product and therefore, with the formation of Tb₂(MoO₄)₃ during the leaching experiments. Furthermore, considering the data shown in Fig. 6, Fig. S7 and Table 6 a similar but slightly weaker effect on the Mo(VI) remobilisation can be seen. This could be interpreted as an indication of a just slightly higher K_{SP} of Tb₂(MoO₄)₃ (compared to the Fe(III) analogue). Another possible explanation for the delayed Mo(VI) remobilisation could be

found in the results reported by (Mancini et al., 2020). As described above, the formation of Fe(III) secondary phases was reported, which in turn could provide new potential sorption sites for Mo(VI). If this assumption is correct, then the same should also apply to Tb(III). However, this leaves one question open: Why do the postulated, already existing Eu(III) secondary phases formed during C-S-H synthesis do not exhibit a comparable effect? Further extensive spectroscopic investigations may help to clarify the dynamics of Mo(VI) remobilisation.

Regarding the lack of influence of Fe(III) and Tb(III) on Eu(III) and U(VI) retention, it is difficult to determine at this point whether: 1) Eu(III) and U(VI) were incorporated “too deep” into the C-S-H structure during synthesis and are therefore not accessible to Fe(III) and Tb(III); 2) Eu(III) and U(VI) occupied other binding sites than Fe(III) and Tb(III); or 3) the binding of Eu(III) and U(VI) is significantly stronger than that of Fe(III) and Tb(III). Point 1) is contradicted by the fact that, for example, ion strength (see above) and PBTC (see below) can influence the remobilisation of Eu(III) or U(VI). This indicates that they should be sensitive to post-synthesis perturbation. Points 2) and 3) are therefore much more likely. In the case of Eu(III), which has itself substituted Ca²⁺ in the interlayers, point 3) seems most likely, which in turn implies that Fe(III) and Tb(III) are not able to displace it. In the case of U(VI), point 2) seems more likely. However, an accurate assessment is not possible at this point, so further investigations are advisable, ideally supplemented by geochemical modelling.

3.6. Influence of PBTC on leaching behaviour

Finally, the influence of PBTC on the leaching behaviour will be discussed. For this purpose, Fig. 7 shows the leaching curves of Mo(VI), Eu(III) and U(VI) under the influence of PBTC. The corresponding concentrations are shown in the supplementary data (Fig. S10). In addition, Table 7 shows the leached relative quantities without, after a 500-fold and after a 1000-fold excess of PBTC; as already mentioned, the excess refers to the initially bound quantity of Eu(III).

Looking first at the leaching of Si(IV) and Ca(II) (Figs. S8 and S9 and Table 7), a clear influence of PBTC can be seen. In the case of Ca(II), up to approx. 30 mL elution volume, less Ca(II) is initially leached compared to ultrapure water (see Fig. S8), whereas considerably more is leached afterwards. In the case of Si(IV) during the whole experiment more Si(IV) is leached with PBTC, than in ultrapure water. However, most interesting in Fig. S8 is the sharp drop in the leached Si(IV) and Ca(II) amount at 180 mL elution volume (600 eq. PBTC). As PBTC is an acid, pH influences are conceivable, but, as Fig. S8 shows, this behaves analogously to the experiments in ultrapure water. Only a very small step is visible at approx. 170 mL. Therefore, only the interaction of PBTC with the analytes themselves is relevant. According to Kretzschmar et al.

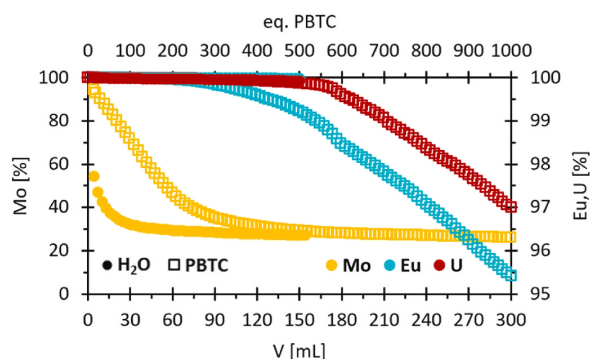


Fig. 7. Remaining Mo(VI), Eu(III) and U(VI) [%] in “WC-L1” sample (see Table 3) plotted against pore water volume during MCE leaching experiment with and without PBTC (in relation to incorporated Eu(III)) injected; without PBTC (dots) same data as shown in Fig. 5.

Table 7

Amounts of remobilised analytes in [%] (in relation to the values listed in Table 3) from “WC L.1” in MCE leaching experiments after the injection of different amounts of PBTC (Data from Fig. 7, S9 and S10); without PBTC same data as shown in Tables 4 and 5; 500-fold excess refers to data in Fig. 7 after 154 mL/500 eq. PBTC; 1000-fold excess refers to data in Fig. 7 after 304 mL/1000 eq. PBTC.

Excess of PBTC (eq. Eu)	Leached amount [%]				
	Si	Ca	Mo	Eu	U
–	8.5	17.1	72.9	0.015	0.076
500	13.9	20.7	71.0	0.807	0.131
1000	20.3	26.3	73.8	4.58	3.00

(2022), at a pH = 10, PBTC is present as a 50/50 mixture of the 4-fold (HL^{4-}) and 5-fold (L^{5-}) deprotonated ligand. From a pH > 11, however, the L^{5-} species dominates (>95 %). Thus, in the measured pH range, many multidentate/chelate complexation reactions with the analytes are conceivable. In addition to the strong complexing properties of PBTC for a variety of metals, basic interactions of PBTC with cement phases, including C–S–H, are also known (Salvadó et al., 1999; Rickert and Thielen, 2004; Spinthaki et al., 2018; Huang et al., 2020). Regarding the incorporated elements, the work of Huang et al. (2020) is very interesting. They functionalised nanoparticles with PBTC and investigated their capacity for a variety of metal ions (including U(VI) and Eu(III)). Under acidic conditions (pH = 4) a capacity of up to 99 mg g^{-1} ($4.16 \cdot 10^{-4} \text{ mol g}^{-1}$) was measured for U(VI) and up to 41 mg g^{-1} ($2.70 \cdot 10^{-4} \text{ mol g}^{-1}$) for Eu(III). However, the higher affinity towards U(VI) should not be given too much importance, as the pH range is completely different from the one here and thus, due to changed speciation the affinity could shift in favour of Eu(III). In the case of the C–S–H–PBTC interactions, Rickert and Thielen (2004) report that PBTC either: 1) partially adsorbs on the C–S–H phases surface; 2) complexes Ca(II) ions; 3) precipitates as a sparingly soluble Ca phosphonate ($\text{Ca}_{2.5}[\text{C}_7\text{H}_6\text{O}_9\text{P}] \cdot x\text{H}_2\text{O}$), which then partially adsorbs on the C–S–H surface, when a certain Ca(II) concentration is reached.

Based on this, the results in Fig. S8 can be interpreted in such a way that PBTC leads to a generally increased C–S–H leaching, whereby the amount of Ca(II) leached exceeds the threshold (not defined in more detail by Rickert and Thielen (2004)) and partly precipitates as $\text{Ca}_{2.5}[\text{C}_7\text{H}_6\text{O}_9\text{P}] \cdot x\text{H}_2\text{O}$. In the case of Si(IV), the threshold defined in Chapter 3.4 seems not to be reached, whereby Si(IV) is not agglomerated/re-retained and is therefore fully remobilised (see Figs. S3 and S8). Based on the data currently available, it is difficult to make a reliable statement about the underlying phenomena for the breakdown of remobilisation at 180 mL (Fig. S8). A possible solution is again offered by Rickert and Thielen (2004). They describe that the $\text{Ca}_{2.5}[\text{C}_7\text{H}_6\text{O}_9\text{P}] \cdot x\text{H}_2\text{O}$ precipitate adsorbed on the surface can form a coating, whereby the C–S–H solid phase is completely enclosed. In that case, the C–S–H phase would no longer be accessible to PBTC, and leaching would consequently collapse.

The hypothesis of the Ca-phosphonate coat is also supported by the U(VI) leaching curve (Fig. 7 and S10). From the point at which C–S–H leaching decreases abruptly, that of U(VI) increases rapidly. At this tipping point, less Ca(II) is available for the formation of possible Ca(II)–PBTC precipitates or complexes, which in turn would lead to more PBTC being available in solution. Due to this shift in equilibrium, U(VI) would now also be complexed and remobilised. However, it must be noted that only the dissolution of a U(VI) secondary phases would be possible at this point, as the C–S–H phases, as described above, are no longer accessible.

In the case of Mo(VI) and Eu(III), the data are again not easy to explain but also support the hypothesis of the Ln(III)–molybdate secondary phase (see Chapter 3.5). As can be seen from Fig. 7 and Fig. S10, the Mo(VI) leaching is significantly slower when PBTC is involved; quite similar to the effect of Fe(III) and Tb(III). If PBTC

remobilises bound Eu(III) (or from secondary phases), this free or complexed Eu(III) could then precipitate with Mo(VI) as $\text{Eu}_2(\text{MoO}_4)_3$. In this case, however, the precipitation as molybdate must be clearly preferential compared to the Eu(III)–PBTC complex. Assuming all this, the increased Eu(III) concentration in Fig. S10 and with that the increasing Eu(III) leaching (Fig. 7) is also well explained, since Eu(III) concentration/remobilisation rises significantly as soon as the one of Mo(VI) drops. Another possible reason for the leaching curves of Mo(VI), and Eu(III), could be delivered by the precipitation of $\text{Ca}_{2.5}[\text{C}_7\text{H}_6\text{O}_9\text{P}] \cdot x\text{H}_2\text{O}$. In that case, a Mo(VI)–Ca(II)–phosphonate–coprecipitate would be suspected and for Eu(III) the same applies as for U(VI): The Ca(II)–phosphonate (or a Mo(VI)–Ca(II)–phosphonate) coat inhibits the accessibility of C–S–H for PBTC, less Ca(II) is available for possible Ca(II)–PBTC precipitates or complexes, more PBTC is available in solution and Eu(III) is now complexed and remobilised. The difference here is, that, compared to U(VI), a stronger PBTC complex have to be formed, since Eu(III) leaching starts earlier (see Fig. 7 and Fig. S10).

The conclusions drawn here should be regarded as preliminary and cannot be fully substantiated based on the data currently available. Here too, additional investigations in combination with geochemical modelling are advisable.

4. Conclusion

In this study, C–S–H phases containing trace amounts of the repository-relevant elements Mo(VI), Eu(III) and U(VI) were synthesised and characterised. An elemental analysis of the supernatant solutions confirmed a successful incorporation of all three elements into the C–S–H phase. X-ray diffractometry showed that the synthesis was successful, and no noticeable impact of the elements added on the C–S–H phases' structure could be identified. ICP–QQQ analysis had shown, that the synthesised C–S–H phases had a C/S ratio of 1.066 ± 0.003 .

The reproducible results derived from standardized batch experiments and MCE with ultrapure water confirmed the expected leaching behaviour for Si(IV) and Ca(II); initially more calcium-followed by coherent leaching. In the case of europium and uranium, in both setups (batch and MCE) quantitative retention was observed, confirming earlier results in the literature. Molybdenum, on the other hand, was remobilised after only a few pore water exchange cycles, although not completely. Two different mechanisms are postulated here: weakly bound adsorption on/in the C–S–H structure and precipitation of CaMoO_4 . These mechanisms had been suspected before, but this is the first time that the hypothesis of both mechanisms has been substantiated with experimental data. In general, the setups showed clear differences. Here, leaching/remobilisation was supposedly stronger pronounced in the batch than in the MCE setup, which can be explained primarily by the state of equilibration and the S/L ratio.

Since MCE are more representative for the conditions in a HLW repository, they were the baseline approach for all further studies. An increase in ionic strength of up to 1 M enhanced both Ca(II) and Si(IV) leaching. At an ionic strength of $I = 2 \text{ M}$, a decrease in leaching for both elements were observed, possibly due to the formation of silicate agglomerates on which calcium could adsorb. This supposed mechanism requires further confirmation by future investigations. A higher ionic strength did not notably impact the remobilisation of Eu(III) and Mo(IV). However, contrary to some literature reports, a slight but significant increase in U(VI) remobilisation at $I = 2 \text{ M}$ could be demonstrated. The cause is postulated to be the release of a Ca(II) mediated U(VI) retention mechanism. This is especially relevant since in HLW repositories, depending on their geochemical conditions, porewaters with high ionic strength of up to $I = 5 \text{ M}$ can be expected. Additional studies with background electrolytes at such ionic strength are therefore recommended.

The addition of the competitive ions Fe(III) and Tb(III) as displacement agents had no influence on the remobilisation dynamics of Eu(III) and U(VI). However, an increase in the Si(IV) and Ca(II) leaching was

observed. Based on those results and the literature available, a substitution of the structure-forming Ca^{2+} ions in the C–S–H phase is suggested. More importantly, the displacement agents delayed and retarded the remobilisation of Mo(VI), which is why the precipitation of insoluble trivalent metal molybdates is proposed.

PBTC as a potential cement additive and complexing agent enhances the leaching of Si(IV), Ca(II), Eu(III) and U(VI), whereas that of Mo(VI) is slightly retarded. During complexation, further interaction mechanisms are also induced. For example, a proposed calcium phosphonate precipitate coating leads to a delayed but rapid U(VI) remobilisation. Furthermore, an earlier remobilisation was observed for Eu(III) compared to U(VI), indicating a preferential complexation of europium. In the case of retarded Mo(VI) remobilisation, co-precipitation molybdenum calcium phosphonates is postulated as a possible reason. However, further studies with appropriate methods to make definite statements are required to confirm the mechanisms of the remobilisation in presence of PBTC.

In summary, this study provides important insights into the retention and dynamic remobilisation of molybdenum, europium, and uranium on C–S–H phases ($\text{C/S} \approx 1$). While it closes critical knowledge gaps and confirms existing hypotheses, it also challenges others. Although currently limited to a single C/S ratio, this work establishes a vital foundation for future geochemical modelling and experimental research, moving us closer to a comprehensive mechanistic understanding of the investigated repository-relevant systems.

CRedit authorship contribution statement

Aaron Haben: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nico Bachmann:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation, Methodology, Visualization. **Jan Jakob Langer:** Writing – review & editing, Writing – original draft, Validation. **Ralf Kautenburger:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the writing process generative-ai

During the preparation of this work the authors used DeepL to help with the translation and wording of some passages. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2026.106684>.

Data availability

Data will be made available on request.

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Behaviour of Mo(VI), Eu(III) and U(VI) in Calcium-Silicate-Hydrate Phases: Immobilisation and Dynamic Remobilisation under Repository-Relevant Conditions

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Supplementary Data

Table S1: Absolute amounts of the analytes in [μmol] bound/incorporated into the C-S-H phases, in the supernatant solution, and on the tube walls involved in the synthesis; the bound amount is calculated from the difference between the amount added during synthesis and the amount quantified in the supernatant and on the tube walls; not detectable (ND).

CSH-Phase	Amount of substance [μmol]														
	Bound/Incorporated					Supernatant					Tube wall				
	Si	Ca	Mo	Eu	U	Si	Ca	Mo	Eu	U	Si	Ca	Mo	Eu	U
U-L	15343	16346	-	-	1.835	3.2	94.8	-	-	ND	2.2	0.3	-	-	0.009
U-H	16190	17212	-	-	19.249	2.0	138.1	-	-	ND	2.1	ND	-	-	0.212
Mo-L	13911	14847	0.992	-	-	2.3	60.0	0.680	-	-	2.4	ND	ND	-	-
Mo-H	17671	18825	11.450	-	-	2.3	114.4	9.792	-	-	2.1	ND	ND	-	-
Eu-L	16363	17470	-	1.924	-	2.4	62.6	-	<0.001	-	2.0	ND	-	0.043	-
Eu-H	14259	15204	-	17.030	-	2.1	74.6	-	<0.001	-	2.1	ND	-	0.109	-
WC-L_1	18490	19720	1.239	2.220	2.221	7.2	105.3	0.985	<0.001	<0.001	4.6	0.2	ND	0.003	0.003
WC-L_2	14966	15954	0.950	1.968	1.839	2.7	81.6	0.718	<0.001	ND	2.6	0.8	ND	0.006	0.006
WC-H	16749	17718	9.438	20.106	20.043	6.0	230.0	10.620	<0.001	<0.001	1.9	ND	0.076	0.027	0.091

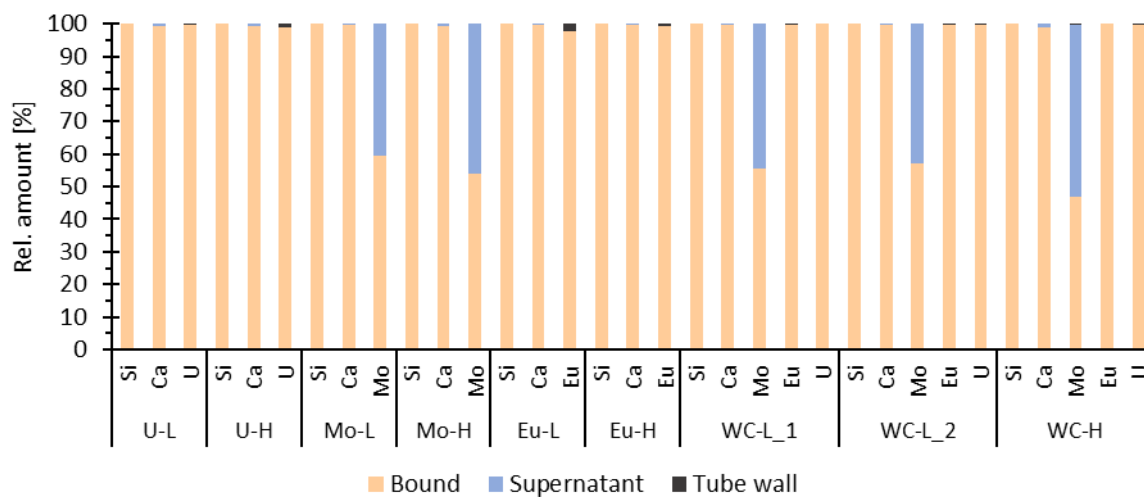


Figure S1: Relative proportion of the amounts of analyte in [%] bound/incorporated in the C-S-H phases, in the supernatant solution, and on the tube walls involved in the synthesis; based on the values shown in Table S1.

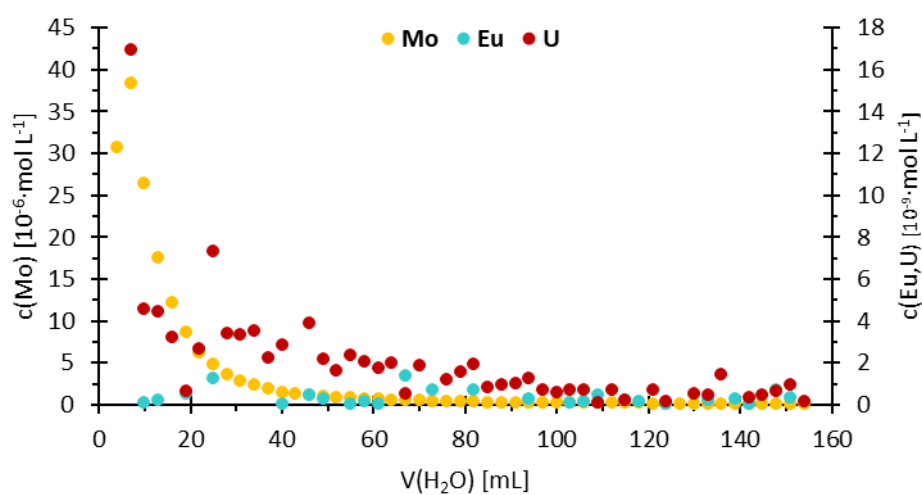


Figure S2: Mo(VI), Eu(III) and U(VI) concentration in eluate of MCE leaching experiment with "WC-H" sample (see Table 3) plotted against ultrapure water volume.

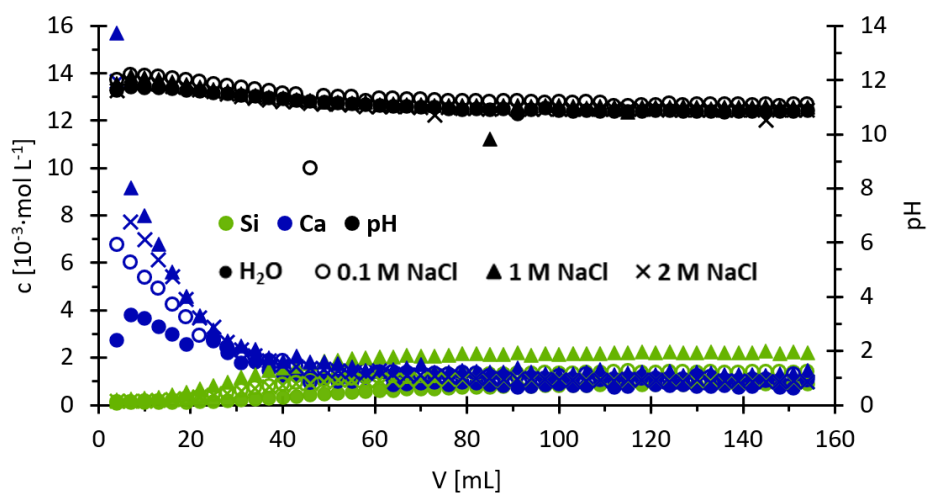


Figure S3: Si(IV), Ca(II) concentration and pH in eluate of MCE leaching experiments with “WC-L_1” sample (see Table 3) plotted against eluent volume in different ionic strength solutions.

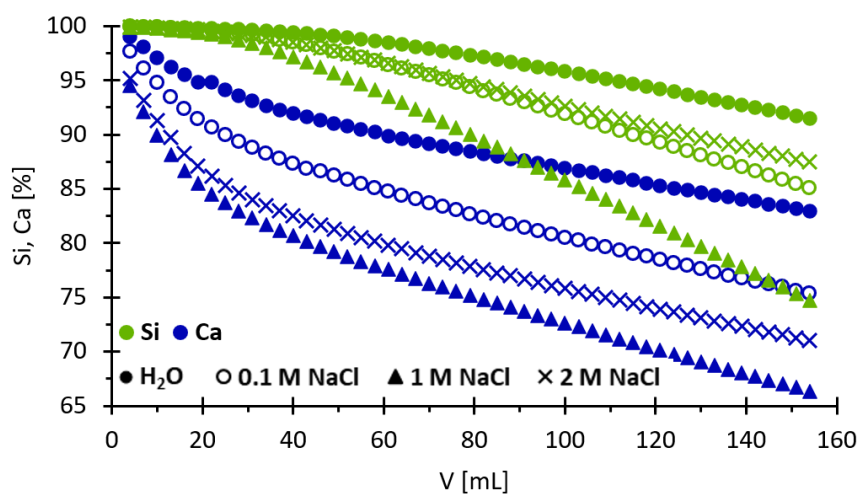


Figure S4: Remaining Si(IV) and Ca(II) [%] in “WC-L_1” sample (see Table 3) plotted against eluent volume in different ionic strength solutions; all were conducted as MCE-leaching experiments.

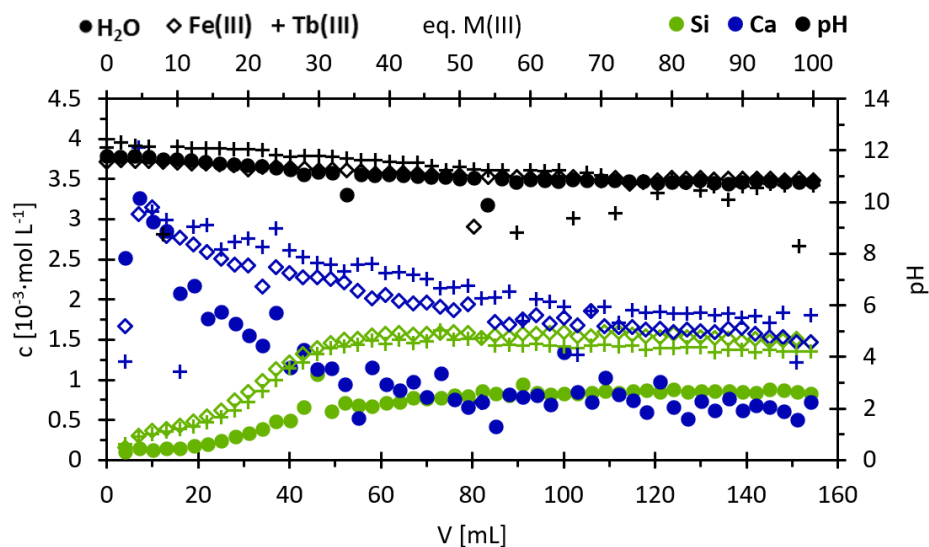


Figure S5: Si(IV), Ca(II) concentration and pH in eluate of MCE leaching experiments with "WC-L_2" sample (see Table 3) plotted against pore water volume with and without M(III) ($M = \text{Fe, Tb}$) as displacement agent; equivalents refer to initial Eu(III) content.

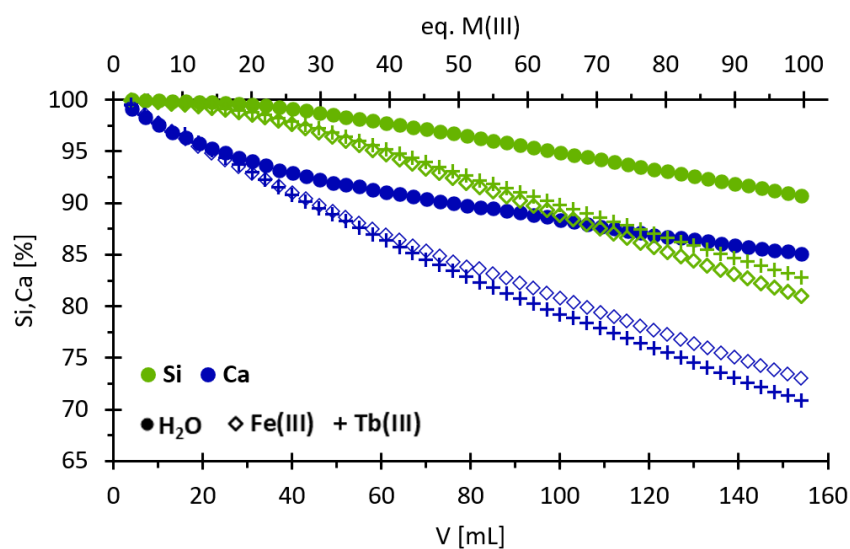


Figure S6: Remaining Si(IV) and Ca(II) [%] in "WC-L_2" sample (see Table 3) plotted against pore water volume during MCE leaching experiment with and without injected displacement agent M(III) ($M = \text{Fe, Tb}$; equivalents in relation to incorporated Eu(III)).

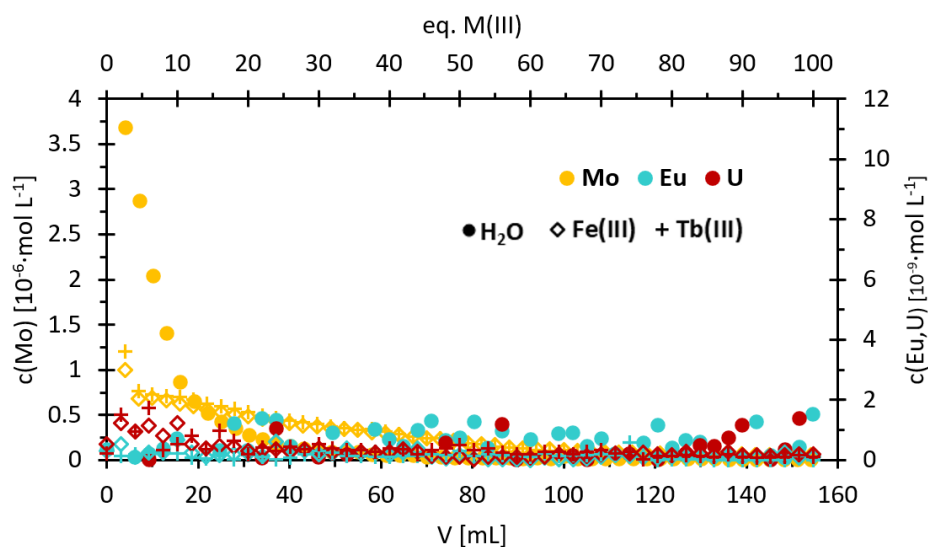


Figure S7: Mo(VI), Eu(III) and U(VI) concentration in eluate of MCE leaching experiments with “WC-L_2” sample (see Table 3) plotted against pore water volume with and without M(III) ($M = \text{Fe, Tb}$) as displacement agent; equivalents refer to initial Eu(III) content.

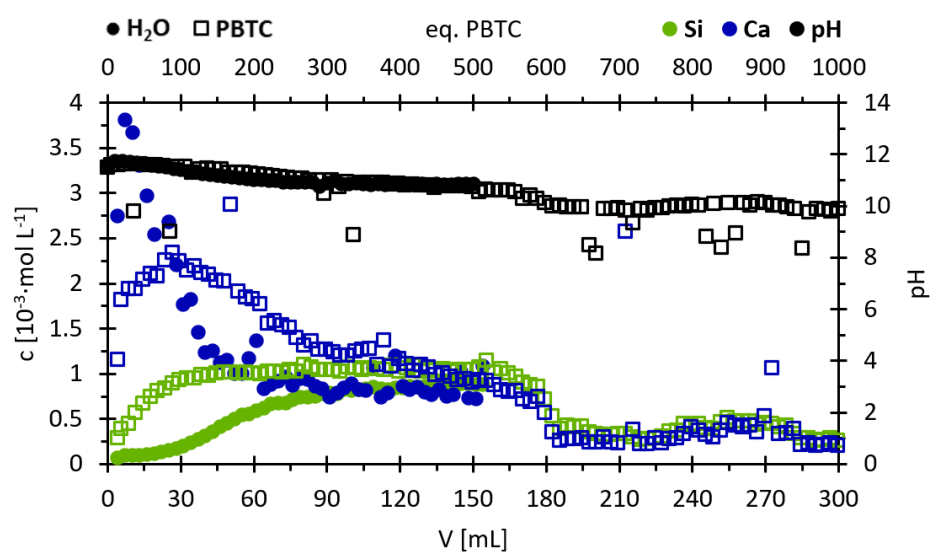


Figure S8: Si(IV), Ca(II) concentration and pH in eluate of MCE leaching experiments with “WC-L_1” sample (see Table 3) plotted against pore water volume with and without PBTC injected; equivalents refer to initial Eu(III) content; without PBTC (dots) same data as shown in Figure S2.

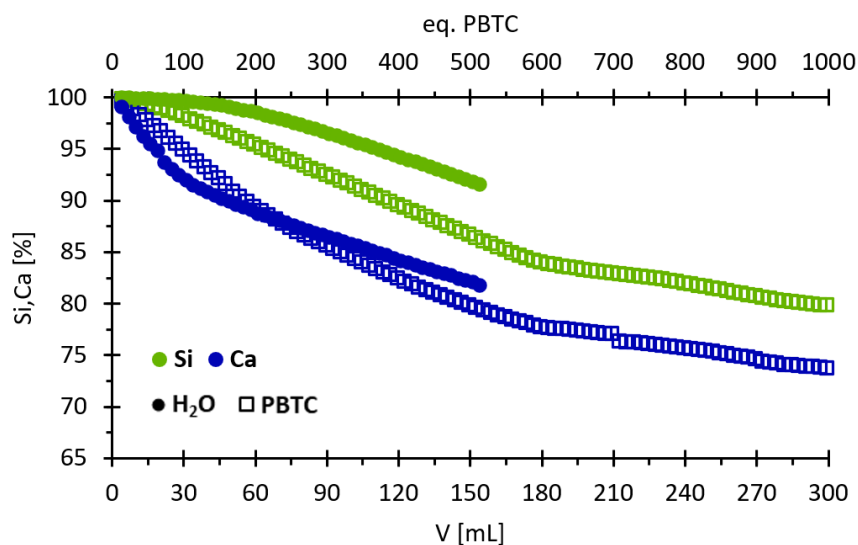


Figure S9: Remaining Si(IV) and Ca(II) [%] in "WC-L_1" sample (see Table 3) plotted against pore water volume during MCE leaching experiment with and without PBTC (in relation to incorporated Eu(III)) injected.

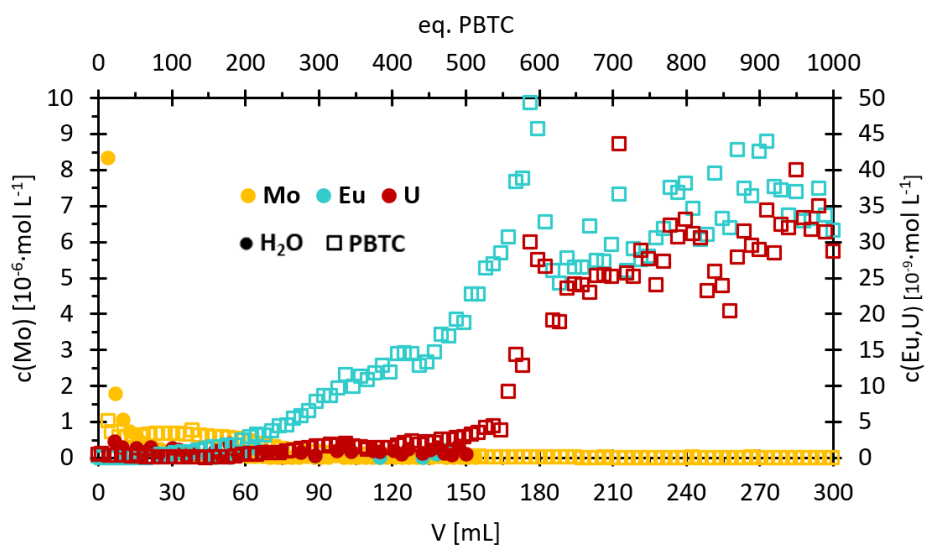


Figure S10: Mo(VI), Eu(III) und U(VI) concentration in eluate of MCE leaching experiments with "WC-L_1" sample (see Table 3) plotted against pore water with and without PBTC injected; equivalents refer to initial Eu(III) content.

3.2 Unpublished results

3.2.1 Implementation of a LA-ICP-MS quantification method for trace elements in repository relevant construction and backfill materials

All the work and references presented so far clearly show that it is common practice to quantify radionuclide retention indirectly via the analyte content in the supernatant solution/eluate. However, it would be immensely advantageous if a direct and spatially resolved quantification in the solid phase (adsorbents) would also be possible. As described in Chapter 2.7.3, a LA-ICP-MS coupling, or in this case a LA-ICP-QQQ, is a versatile and very powerful analytical method to quantify trace elements in solid phases. It therefore makes sense to establish such a method for quantifying traces of repository-relevant elements in also repository-relevant solid phases, like C-S-H phases. This chapter describes two of the methods already mentioned in Chapter 2.7.3: external calibration using matrix-matched C-S-H RMs produced in-house and an adaptation of the “dual sample/standard approach” according to O'Connor et al. [168] for the rapid quantification of element ratios.

3.2.1.1 External LA-ICP-QQQ calibration for trace elements in C-S-H Phases

In the case of routine analyses, it is useful to have matrix-matched standard materials available. This enables fast and accurate analysis of the desired solid phase, even at high throughput. As can be seen above, the solid phase most frequently investigated for this work is C-S-H. Therefore, as part of the contribution to repository research, it is understandable to establish a routine LA-ICP-MS/-QQQ method for quantifying repository relevant trace elements in C-S-H phases. For this reason, this chapter will now describe the approach to develop a method for preparing C-S-H standard materials (C-S-H RMs) and a method for LA-ICP-QQQ analysis using these RMs.

This chapter describes, among other things, the production of four different C-S-H RMs. To produce these RMs, the schematic routine described in Figure 23 is followed. During that always 500 mg of the respective C-S-H phase was suspended in a solution containing a known concentration of all analytes. Depending on the RMs prepared the C-S-H phase was prior to that ether ball milled or not. The suspending was followed by drying in an oven overnight. For optimal homogeneous distribution of the analytes in the solid material, the dried solid phases were ground in a planetary ball mill (PBM) and then pressed into pellets. The decisive parameters for any optimisations of the manufacturing process, like the S/L ratio of the initial suspension, the grinding/milling time, and the milling speed are given in Table 6. In all cases, the same PBM was used (Planetary Micromill Pulverisette 7, Fritsch, Idar-Oberstein, Germany). The manufacturer's specifications for the standard solutions used can be found in Table_A 1 (in the appendix). Various multi-element standard solutions were used to prepare the individual RMs – e.g. for Circosil®_CG: Since the S/L ratio was set to 1 g mL⁻¹, a 100 mg L⁻¹ solution resulted in a 100 µg g⁻¹ standard, a 75 mg L⁻¹ solution resulted in a 75 µg g⁻¹ standard, etc.

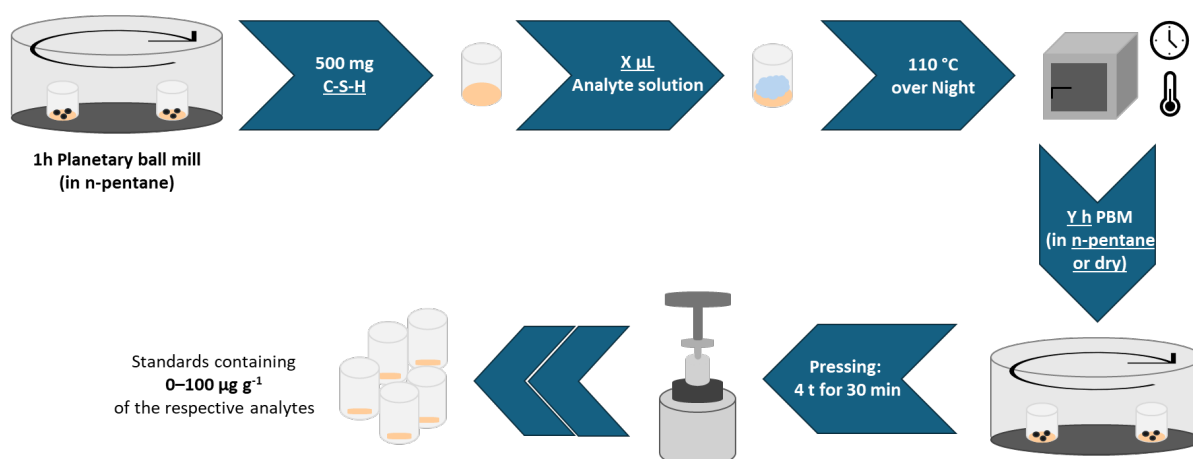


Figure 23: Schematic illustration of the preparation routine for all C-S-H RMs (schematic drawing adapted from Celine Güttler, former group member); 10 mL agate jar and 3 agate balls with $\varnothing = 10$ mm, milling speed = 4, stamp $\varnothing = 10$ mm.

Table 6: Conditions for the preparation routine of the various C-S-H RMs shown in Figure 23; with the analytes contained in the respective RMs, the volume of the added analyte solution ($V(X)$), the grinding time in the PBM ($t(Y)$) and the final concentrations of the analytes in the solid.

RM	Analytes	PBM prior	$V(X)$ [μL]	$t(Y)$ [h]	PBM conditions	Concentrations [$\mu\text{g g}^{-1}$]
Circosil®_CG	Y, Zr, Mo, Ru, Pd, Cs, Sm, Eu, Ho, U	No	500	2	dry	0, 1, 10, 30, 50, 70, 100
syn C-S-H_1	Sc, Y, Zr, Mo, Ru, Pd, Cs, Sm, Eu, Ho, U	No	5.500	1	n-pentane	0.1, 2.5, 5, 10, 50, 100
syn C-S-H_2	Mo, Eu, U	No	500	2	n-pentane	0, 1, 10, 50, 100
syn C-S-H_3	Mo, Eu, U	Yes	4.500	1	n-pentane	0, 1, 10, 50, 100

A schematic illustration of the LA-ICP-QQQ coupling technique is illustrated in Figure 24, showing the used ESI Elemental Scientific Lasers NWR213 LA ($\lambda = 213$ nm, Bozeman, Montana, USA) and the Agilent 8900 ICP-QQQ (Santa Clara, USA). The material is ablated in the ablation chamber and flushed out of the chamber by an 800 mL min^{-1} He gas flow. Shortly after the ablation chamber, the He aerosol flow is mixed with an Ar gas flow. This is fed from the nebuliser gas outlet of the ICP-QQQ (1.0 L min^{-1}) to accelerate aerosol transport and stabilise the plasma. The He-Ar-aerosol stream is then ultimately fed directly into the torch of the ICP-QQQ.

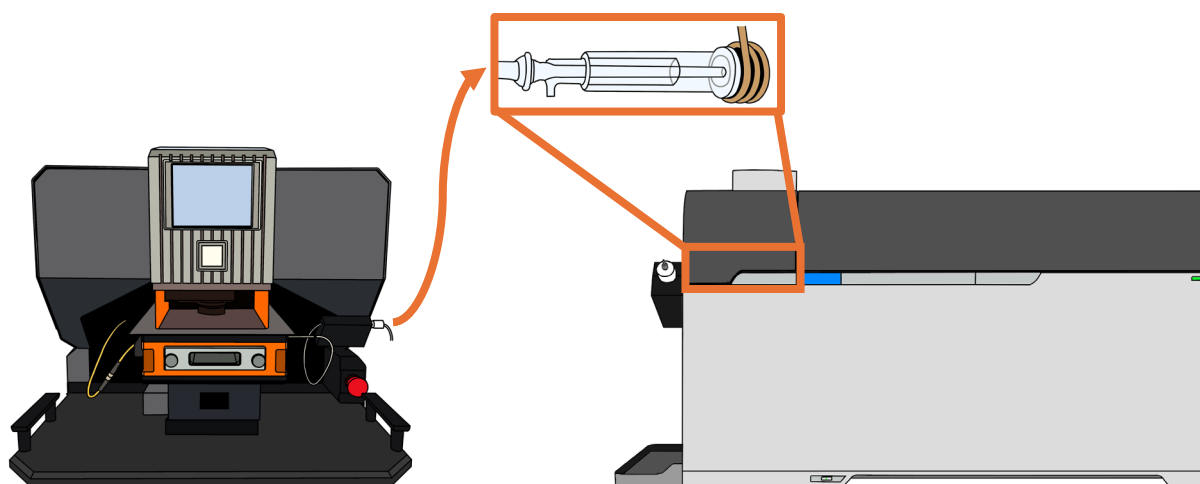


Figure 24: Schematic Drawing for a general setup for a LA-ICP-QQQ analysis; with NWR213 LA and the 8900 ICP-QQQ.

In the course of optimising/establishing the LA-ICP-QQQ method, initial investigations were conducted by Celine Güttler (former member of the working group). Part of these preliminary investigations involved optimising the laser power and the manufacturing routine (see Figure 23). As a key metric for evaluating the quality of the manufacturing process, the spiked analytes in the standard materials were measured using the LA-ICP-MS method and the relative standard deviation (RSD) in [%] of the signals were determined. These serve both as a measure of the homogeneity of the analytes in the solid material and as an indicator of the suitability of the selected laser parameters. For example, poor homogeneity and excessive laser energy density/fluence result in an increased RSD. The respective RSDs were obtained by recording the averaged time-resolved analyte signals (TRA) in the MassHunter ICP-QQQ software (version 5.2 D.01.02) – the software then calculates the RSD automatically. As a result of these preliminary investigations, Celine Güttler concluded that the ideal manufacturing conditions correspond to those of the Circosil®_CG RMs (in Table 6). The RSD values obtained ranged between 5% and 6%. The measurement parameters that were also optimised are as follows: 1150 W plasma power, 0.1 s integration time, 5 J cm⁻² laser power, 10 Hz sampling rate, 10 µm s⁻¹ scan speed, 50 x 50 µm spot size and 2.0 mm long ablation lines.

To make a clear distinction: this is where Celine Güttler's work ended. Based on the Circosil®_CG RMs she produced, initial attempts were made to quantify Mo, Eu, and U in one of incorporated C-S-H phases described in Chapter 3.1.3. To be more precise: for all future investigations, a pellet was pressed from the WC-L_2 C-S-H phase (stamp Ø = 10 mm, 4 t for 30 min). The preparation routine, quantification method and the resulting analyte concentrations of the WC-L_2 sample can be found in the publication presented in Chapter 3.1.3. The molar concentrations determined indirectly from the supernatant solution (listed in publication Table 3) can be converted into the following mass concentrations: C(Mo) = 48.9 µg g⁻¹, C(Eu) = 149.9 µg g⁻¹ and C(U) = 219.2 µg g⁻¹. For the LA-ICP-QQQ-analysis, always 2 mm long lines were ablated on the RM and the sample material, and the respective signals were further processed using the Iolite software (Version: v4.10.4). Figure 25 shows a screenshot (from Iolite) with the TRA data for the analysis of the WC-L_2 sample using the Circosil®_CG RMs. For further calculations, the signal plateaus shown in Figure 25 (resembling the 2 mm ablation

lines) are averaged and the standard deviation is calculated. Those averaged values are then used to plot the calibration curves and to calculate the analyte contents.

Based on the TRA data shown in Figure 25 the RSD values of the measurement signals were calculated (Table 7), the calibration curves for the analytes Mo, Eu, and U were derived (Figure 26), and finally the concentrations of the analytes in the solid were calculated. These were then compared with the true/known values, and the resulting deviations were calculated (Table 8).

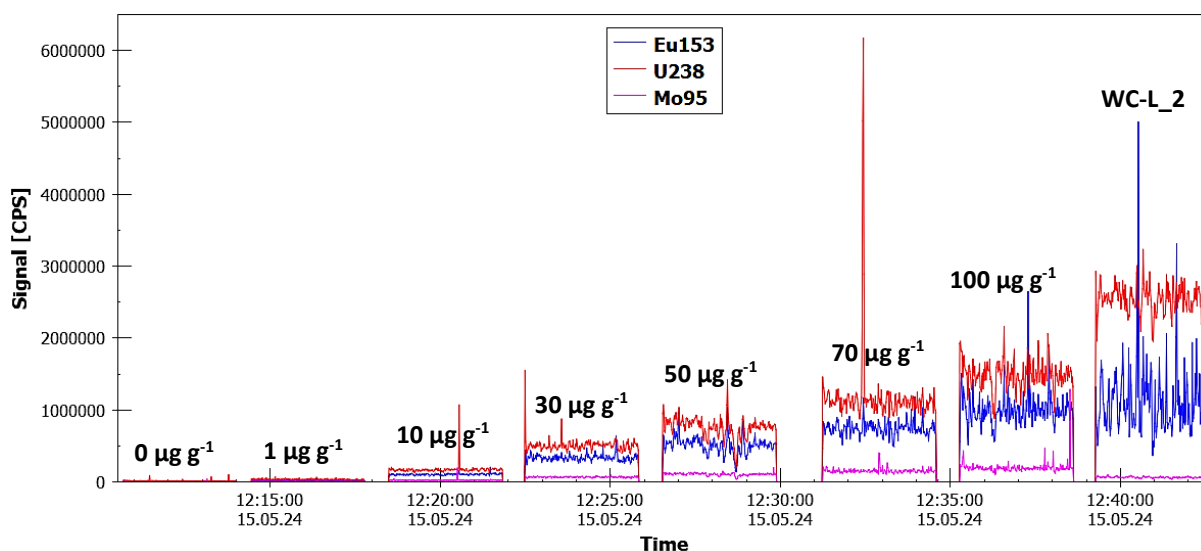


Figure 25: Screenshot the Lolite software (version: v4.10.4) showing the Mo, Eu and U TRA data resulting from the analysis of the WC-L_2 sample using *Circosil*[®]_CG RMs; measurement conditions see Table 7.

Table 7: RSD values for all incorporated analytes of the *Circosil*[®]_CG RMs derived from calibration described in Figure 25 and Figure 26; 1150 W, [NoGas], 0.1 s integration time, 5 J cm⁻², 10 Hz, 10 µm s⁻¹, 50 x 50 µm spot size, 2.0 mm ablation lines.

C _{Analytes} [µg g ⁻¹]	0	1	10	30	50	70	100
RSD [%]	6–22	2–10	1–2	1–2	2–3	1–2	1–3

Based on the RSD values, correlation coefficients (R^2), and error bars shown in Table 7 and Figure 26, a successful calibration can be assumed at first glance. As already mentioned, for better validation, the Mo, Eu, and U contents in the incorporated C-S-H phase (WC-L_2) were determined using the calibration curves obtained. These concentrations, determined using LA-ICP-MS, can then be compared with the known values and the deviations calculated (see Table 8).

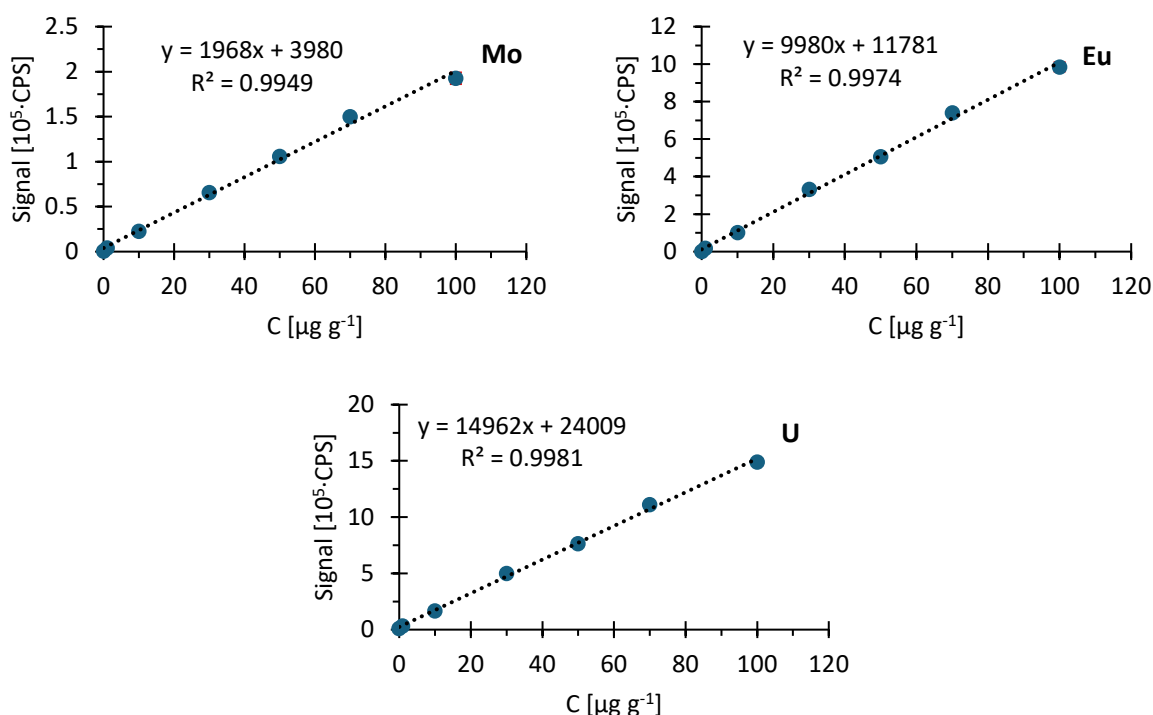


Figure 26: Calibration curves for Mo, Eu and U resulting from the **Circosil®_CG RMs** described in Table 7 and Figure 25; measurement conditions see Table 7.

Table 8: Analyte concentration in the **WC-L_2** sample, the calculated concentration derived from the LA-ICP-MS measurement (Figure 25 / Figure 26) using **Circosil®_CG RMs** and the resulting deviations [%]; measurement conditions see Table 7.

	Mo	Eu	U
C_{WC-L_2} [$\mu\text{g g}^{-1}$]	45.9	149.9	219.2
C_{LA-ICP-MS} [$\mu\text{g g}^{-1}$]	29.6	107.5	168.9
Deviation [%]	-35.5	-28.3	-22.9

As shown in Table 8, the quantified analytes were significantly underestimated. No normalisation was performed at this point, as it was assumed that the matrices were sufficiently identical. However, this does not appear to be the case. A purely visual comparison of the $100 \mu\text{g g}^{-1}$ Circosil®_CG RM with the pressed WC-L_2 sample revealed a slightly darker coloration of the RM. It should be noted here that a Circosil® matrix was used for the RMs ($C/S = 0.65\text{--}0.83$, see Chapter 2.4), while the WC-L_2 sample was produced in the laboratory scale with a C/S ratio of 1.07 [8] (see Chapter 3.1.3). Thus, the first approach to counteract the underestimation was to produce RMs with the same matrix. For this purpose, C-S-H phases were used that were synthesised analogue to WC-L_2, but without the incorporated analytes Mo, Eu, and U (syn C-S-H; synthesis analogue to Chapter 3.1.3 [8]). The preparation routine of the syn C-S-H_1 RMs ($0.1, 2.5, 5, 10, 50$ and $100 \mu\text{g g}^{-1}$) can again be found in Table 6. The added analyte solution contained Sc, Y, Zr, Mo, Ru, Pd, Cs, Sm, Eu, Ho, and U. This was added in accordance with the preparation method for the Circosil®_CG RMs, whereby 5 mL of ultrapure water was added to improve

initial homogeneity (total 5.500 μL , previously 500 μL). Furthermore, the grinding conditions in the PBM were adjusted: wet grinding in n-pentane was performed for 1 h (previously 2 h dry).

A short note at this point: Usually, when developing new methods, the analysis/device parameters (e.g. laser settings) are optimised first – as was done by Celine Güttler. As it will become apparent later, there is still room for optimisation, but at this point, it seemed more likely that the cause of the high deviations lied in the manufacturing routine (the matrix material). Therefore, initial optimisation attempts were also being made in this regard.

Using the *syn C-S-H_1* RMs, LA-ICP-MS quantification of the Mo, Eu, and U concentration in the *WC-L_2* sample was then performed. Data processing and evaluation were performed as described above: averaging signal plateaus in Iolite, calculation of the RSD, plotting the calibration curves, and calculation of the respective concentrations. The resulting RSD of the measured values, calibration curves, and calculated concentrations, including deviations, are shown in Table 9, Table 10, and Figure 27.

Table 9: RSD values for all incorporated analytes of the *syn C-S-H_1* RMs derived from calibration described in Figure 27; 1150 W, [NoGas], 0.1 s integration time, 5 J cm^{-2} , 10 Hz, 10 $\mu\text{m s}^{-1}$, 50 x 50 μm spot size, 2.0 mm ablation lines.

$C_{\text{Analytes}} [\mu\text{g g}^{-1}]$	0.1	2.5	5	10	50	100
RSD [%]	3–30	1–2	1–3	3–6	1–4	1–3

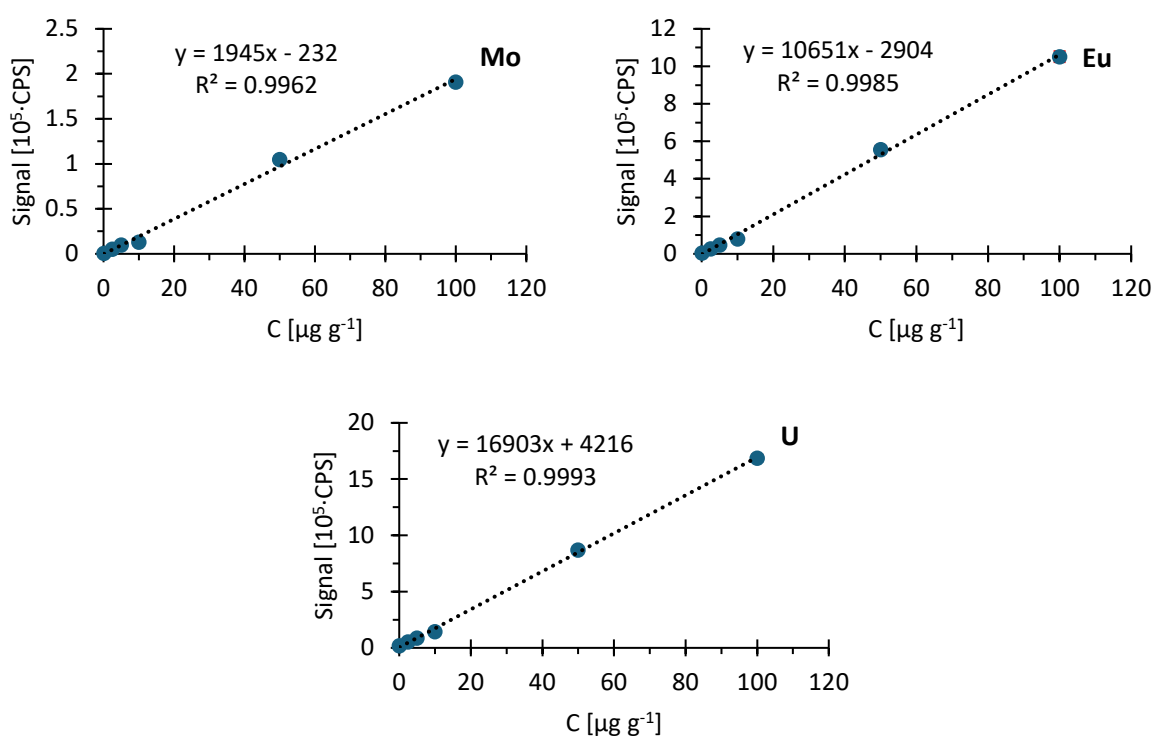


Figure 27: Calibration curves for Mo, Eu and U resulting from the *syn C-S-H_1* RMs; measurement conditions see Table 9.

Again, based on the RSD values, correlation coefficients (R^2), and error bars shown in Table 9 and Figure 27, a successful calibration can be assumed. Based on the R^2 values, one could even argue for a better calibration curve (0.9962 vs. 0.9949, 0.9985 vs. 0.9974, and 0.9993 vs. 0.9981). Analogue to above, the Mo-, Eu- and U-concentrations in the WC-L_2 sample, determined using LA-ICP-MS, is calculated and compared with the known values (see Table 10).

Table 10: Analyte concentration in the **WC-L_2** sample, the calculated concentration derived from the LA-ICP-MS measurement (Figure 27) using **syn C-S-H_1 RMs** and the resulting deviations [%]; measurement conditions see Table 9.

	Mo	Eu	U
C_{WC-L_2} [$\mu\text{g g}^{-1}$]	45.9	149.9	219.2
C_{LA-ICP-MS} [$\mu\text{g g}^{-1}$]	35.1	111.7	189.2
Deviation [%]	-23.5	-25.5	-13.7

Despite using the same matrix, LA-ICP-MS analysis with the **syn C-S-H_1 RMs** still results in high underestimations – albeit slightly lower than with the **Circosil®_CG RMs** (see Table 8 and Table 10), but still unacceptable. Similar to the **Circosil®_CG RMs**, slight colour differences between the **syn C-S-H_1 RMs** and the sample were also be seen (RM marginally darker). These were particularly noticeable at the two highest concentrations (50 and 100 $\mu\text{g g}^{-1}$). An underestimation of the analytes in the sample results from the detection of larger amounts of analytes in/from the RMs. Assuming accurate working practices, a higher ablation efficiency of the RMs can be concluded. Based on the slightly darker coloration of the **C-S-H_1 RMs** at concentrations of 50 and 100 $\mu\text{g g}^{-1}$, a better absorption of the laser light can be assumed. To advance the further method development, this effect must be better understood, at least to some extent. Therefore, the measurement was repeated, but this time only up to a **C-S-H_1 RM** concentration of 10 $\mu\text{g g}^{-1}$. As above, the resulting RSD of the measured values, calibration curves, and calculated concentrations, including deviations, are shown in Table 11, Table 12, and Figure 28.

Again, a short note at this point: It can certainly be argued that, given this problem, it would be appropriate to normalise the analyte signals to one, or even the sum, of the structure-forming elements Ca and Si. In theory, this should compensate (to a certain extent) differences in ablation efficiency between the RM and sample material. However, the aim of further investigations was to identify the reasons for the differences, which is why normalisation was not applied.

Table 11: RSD values for all incorporated analytes of the **syn C-S-H_1 RMs** derived from calibration described in Figure 28; 1150 W, [NoGas], 0.1 s integration time, 5 J cm^{-2} , 10 Hz, 10 $\mu\text{m s}^{-1}$, 50 x 50 μm spot size, 2.0 mm ablation lines.

C_{Analytes} [$\mu\text{g g}^{-1}$]	0.1	2.5	5	10
RSD [%]	3–27	1–2	2–3	3–6

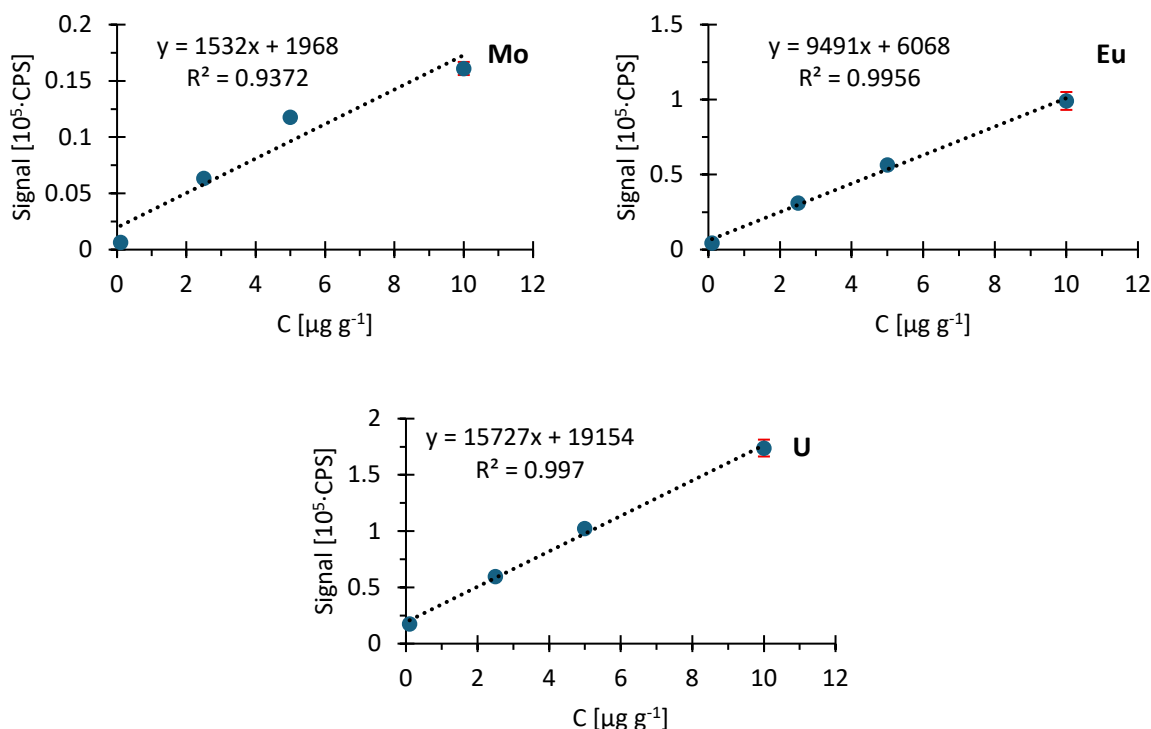


Figure 28: Calibration curves for Mo, Eu and U resulting from the **syn C-S-H_1 RMs** measurement conditions see Table 11.

Table 12: Analyte concentration in the **WC-L_2** sample, the calculated concentration derived from the LA-ICP-MS measurement (Figure 28) using **syn C-S-H_1 RMs** and the resulting deviations [%]; measurement conditions see Table 11.

	Mo	Eu	U
C_{WC-L_2} [$\mu\text{g g}^{-1}$]	45.9	149.9	219.2
C_{LA-ICP-MS} [$\mu\text{g g}^{-1}$]	50.3	149.4	217.1
Deviation [%]	9.6	-0.3	-1.0

Without the highest concentrations of syn C-S-H_1 RMs, a very good, almost perfect recovery of the analytes in the WC-L_2 sample was achieved; just the 9.6% overestimation for Mo is not ideal but acceptable. Since the exclusion of the syn C-S-H_1 RMs, which differed visually from the sample material, led to a significant improvement in recovery, it can be assumed that whatever caused the colouring is the reason for the differing ablation efficiency. Considering the identical matrix material and that the effect is more pronounced at higher concentrations, the additional incorporated elements must be the reason.

The next logical step was therefore to adjust the RM preparation process in that way, that both the matrix and the incorporated elements are identical. Table 6 shows the process for the syn C-S-H_2 RM preparation, which only content Mo, Eu, and U. Due to possible carryovers, the preparation of the standard suspension was reconsidered, which is why only 500 μL (as at the beginning) of analyte solution was added to the dry solid phase. To compensate for this initial homogenisation, the milling

time was again extended to 2 h but in n-pentane. Otherwise, the preparation was conducted analogue to the previous ones, using multiple solutions with different analyte concentrations.

The syn C-S-H_2 RMs were used in the same way as above to quantify the Mo, Eu, and U contents in the WC-L_2 sample. Three analyses were performed, with the best results presented in the usual manner in Figure 29 (calibration curves) and Table 13 (calculated concentrations and deviations from the known values). Since the RSD values do not differ significantly from those of the other RMs, they will not be listed explicitly if this remains the case.

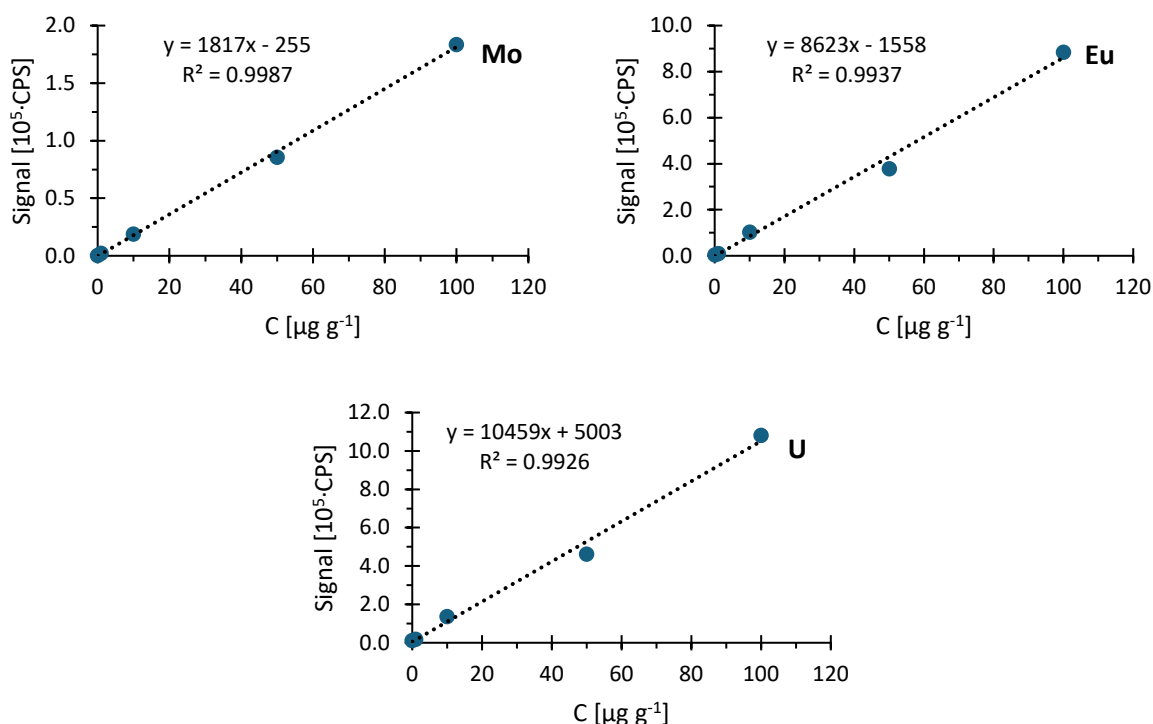


Figure 29: Calibration curves for Mo, Eu and U resulting from the **syn C-S-H_2 RMs**; 1150 W, [NoGas], 0.1 s integration time, 5 J cm⁻², 10 Hz, 10 $\mu\text{m s}^{-1}$, 50 x 50 μm spot size, 2.0 mm ablation lines.

Table 13: Analyte concentration in the **WC-L_2** sample, the calculated concentration derived from the LA-ICP-MS measurement (Figure 29) using **syn C-S-H_2 RMs** and the resulting deviations [%]; measurement conditions see Figure 29.

	Mo	Eu	U
C_{WC-L_2} [$\mu\text{g g}^{-1}$]	45.9	149.9	219.2
C_{LA-ICP-MS} [$\mu\text{g g}^{-1}$]	37.1	124.2	191.8
Deviation [%]	-19.2	-17.1	-12.5

In the calibration range from 0 to 100 $\mu\text{g g}^{-1}$, using the syn C-S-H_2 RMs provides the best results (see Table 8, Table 10 and Table 13). However, one problem remains: like the syn C-S-H_1 RMs, excluding the RM with the highest concentration (100 $\mu\text{g g}^{-1}$) also leads to a significant improvement in recovery.

In the best case, deviations of -1.6% (Mo), -4.7% (Eu), and 7.6% (U) were achieved with the syn C-S-H₂ RMs in a calibration range of 0–50 µg g⁻¹.

At this point, it was difficult to further optimise the preparation routine of the RMs (already same matrix and same analytes). However, considering the theory outlined in Chapter 2.7.3, it is conceivable that adjusting the laser settings could lead to a better result. The laser settings developed by Celine Güttler were used in all the analyses described above. At this point, however, it must be assumed that these are not optimal for the analysis. Therefore, the analysis of the WC-L₂ sample using the syn C-S-H₂ RMs was repeated with an increased laser power (fluence) of 7 J cm⁻², instead of the previous 5 J cm⁻². Once again, the results are presented in the usual manner in Figure 30 (calibration curves) and Table 14 (calculated concentrations and deviations from the known values).

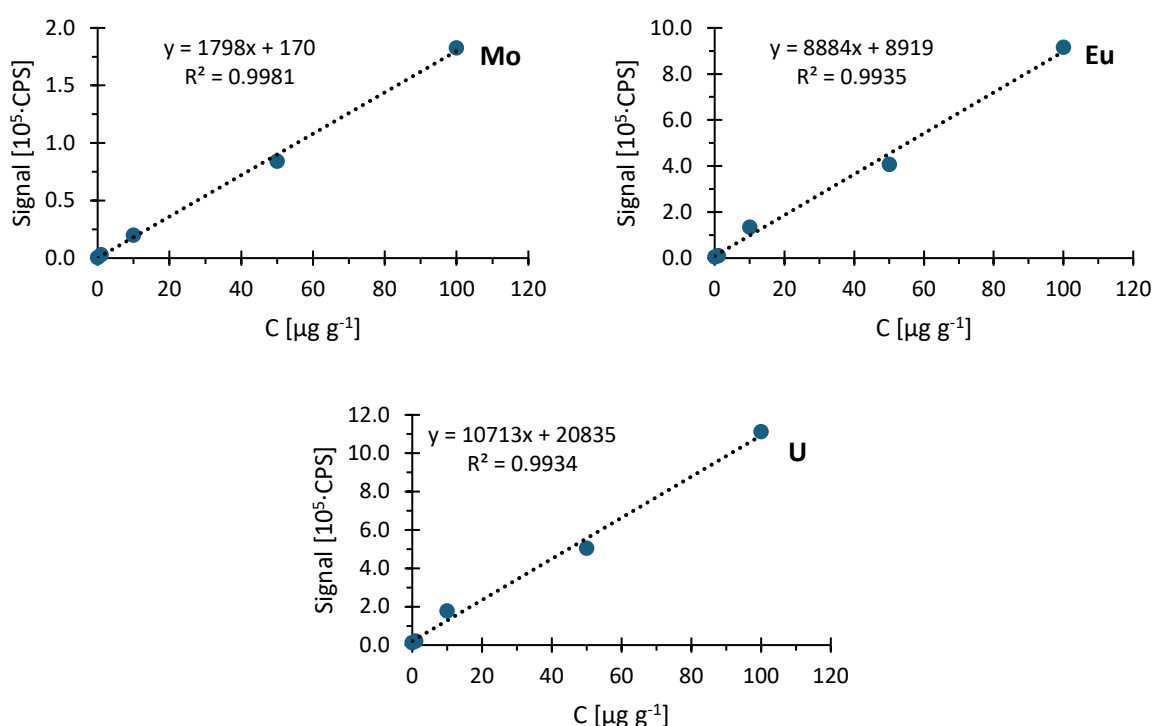


Figure 30: Calibration curves for Mo, Eu and U resulting from the **syn C-S-H₂ RMs**; 1150 W, [NoGas], 0.1 s integration time, 7 J cm⁻², 10 Hz, 10 µm s⁻¹, 50 x 50 µm spot size, 2.0 mm ablation lines.

Table 14: Analyte concentration in the **WC-L₂** sample, the calculated concentration derived from the LA-ICP-MS measurement (Figure 30) using **syn C-S-H₂ RMs** and the resulting deviations [%]; measurement conditions see Figure 30.

	Mo	Eu	U
C_{WC-L₂} [µg g⁻¹]	45.9	149.9	219.2
C_{LA-ICP-MS} [µg g⁻¹]	46.3	149.6	232.2
Deviation [%]	0.9	-0.2	5.9

As can be seen from Figure 29 and Figure 30, a higher fluence had no significant influence on the R^2 values of the calibration curves, but it did have an influence on the recovery. Now, using the entire calibration range ($0\text{--}100\ \mu\text{g g}^{-1}$), an excellent recovery was achieved (see Table 14). Accordingly, the laser power is the decisive parameter for achieving the best possible calibration result. Therefore, the effects of different fluences on the analyte recovery will be investigated in the following. For this purpose, analyses of the elements Mo, Eu, and U in the WC-L_2 sample were performed using the syn C-S-H_2 RMs at different fluences ($3\text{--}10\ \text{J cm}^{-2}$) and the deviations (analogous to above) were calculated for each case. In the fluence range investigated, it should thus be possible to determine an optimal value for the laser power.

A total of 4 fluence-dependent analyses of the WC-L_2 sample were performed using the syn C-S-H_2 RMs in the fluence range from 3 to $10\ \text{J cm}^{-2}$. The calculated Mo, Eu, and U concentrations, the calculated deviations, R^2 values of the respective calibration curves, and the averaged RSD values are listed in Table_A 2, Table_A 3, Table_A 4 and Table_A 5 in the appendix. For better presentation of the points being made, the averaged values for the individual fluences are shown in Table 15.

Table 15: Averaged concentrations of Mo, Eu, and U, averaged deviations from the known values in the **WC-L_2** sample ($45.9\ \mu\text{g g}^{-1}$ Mo, $149.9\ \mu\text{g g}^{-1}$ Eu and $219.2\ \mu\text{g g}^{-1}$ U) and averaged R^2 values using the **syn C-S-H_2** RMs at different laser powers (fluence = $3\text{--}10\ \text{J cm}^{-2}$); based on values in Table_A 2, Table_A 3, Table_A 4 and Table_A 5.

Fluence	Avg. C _{Calculated} [$\mu\text{g g}^{-1}$]			Avg. deviation [%]			Avg. R^2		
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U
3	36.5	124.6	190.7	-20.5	-16.9	-13.0	0.9944	0.9909	0.9901
4	36.0	123.5	196.8	-21.5	-17.6	-10.2	0.9870	0.9908	0.9904
5	39.4	140.6	205.2	-14.2	-6.2	-6.4	0.9956	0.9907	0.9910
6	42.6	136.5	225.3	-7.1	-8.9	2.8	0.9946	0.9912	0.9915
7	47.4	148.9	245.7	3.4	-0.7	12.1	0.9975	0.9946	0.9949
8	51.0	168.1	260.8	11.2	12.2	19.0	0.9981	0.9971	0.9975
9	52.0	161.7	260.5	13.3	7.9	18.9	0.9991	0.9964	0.9969
10	51.4	165.0	266.7	12.1	10.1	21.7	0.9987	0.9957	0.9964

Several very interesting conclusions can be drawn from the values shown in Table 15: The best recovery is obtained at fluences of 6 and $7\ \text{J cm}^{-2}$. It is also noticeable that severe underestimation is observed at fluences $< 6\ \text{J cm}^{-2}$ and severe overdetermination at fluences $> 7\ \text{J cm}^{-2}$. This confirms the previous assumption that the ablation efficiencies of the sample and RMs behave differently depending on the fluence.

Figure 31 shows schematically how the signals of a matrix matched standard and a sample behave with increasing fluence in the analyses performed here. The ideal progression is shown on the left: both the RM signal and that of the sample should respond equally to increasing fluence. The actual case is shown on the right: when plotting the signal development as a function of fluence, the curves of the RM and the sample behave differently. Based on this observation, where the two straight lines meet, there

should be equal ablation efficiency of the materials. If this assumption is applied to the analysis presented in Table 15, and the data of one selected RM is plotted analogously to Figure 31, they should intersect somewhere between 6 and 7 J cm^{-2} . To test this hypothesis, the measurement data from the analysis shown in Table_A 4 were processed as follows: Both, the measurement signals from the 100 $\mu\text{g g}^{-1}$ syn C-S-H_2 RM and those from the WC-L_2 sample were normalised to the corresponding concentration for Mo, Eu, and U, and plotted against the fluence. The resulting diagrams are shown in Figure 32.

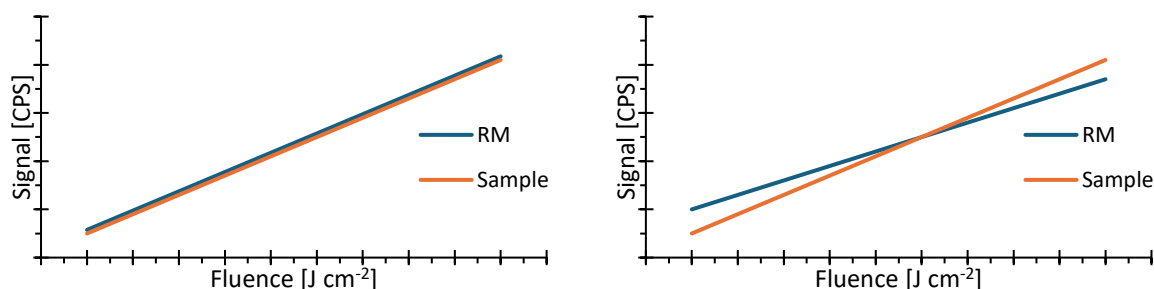


Figure 31: Hypothetical signal plotted against the fluence; Left: the ideal (expected) signal curve of a matrix-matched standard and the sample; right: the signal curve as a function of the fluence of the RMs produced here and the WC-L_2 sample.

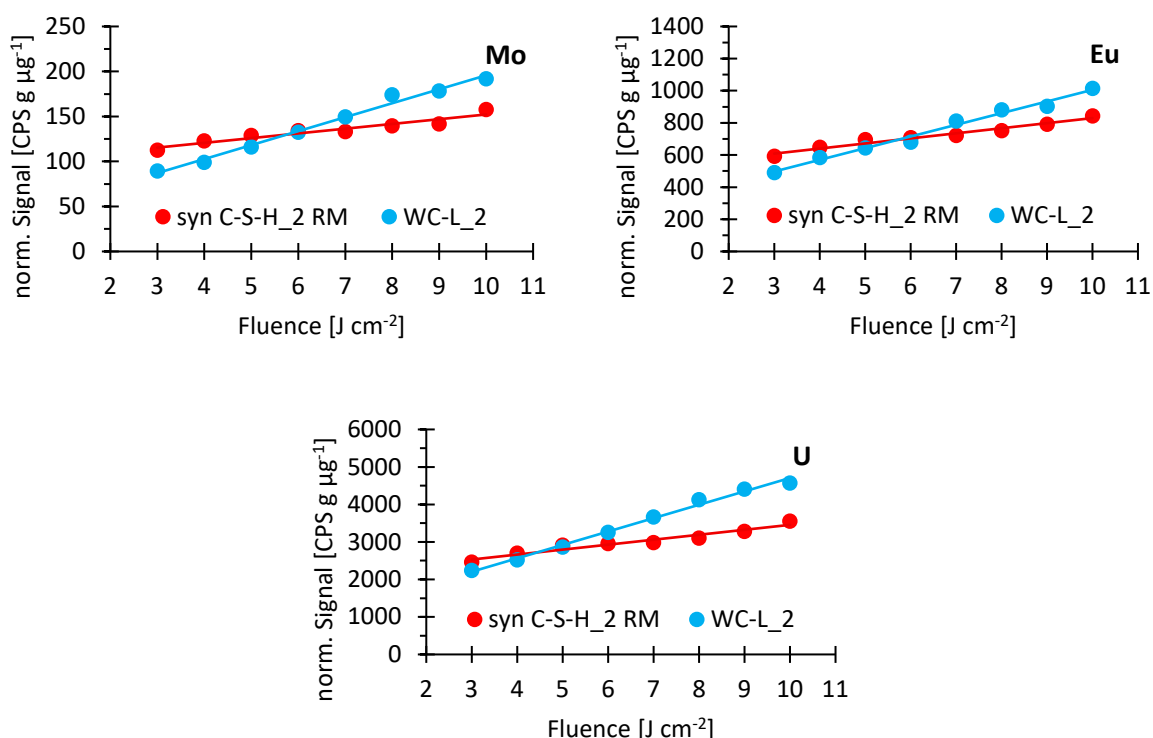


Figure 32: The measurement signals normalised to the respective concentration (in solid) for Mo, Eu, and U of the 100 $\mu\text{g g}^{-1}$ syn C-S-H_2 RM and the WC-L_2 sample plotted against the fluence used during the analysis; measurement conditions see Table_A 4.

Figure 32 now definitively proves the assumption: The syn C-S-H₂ RMs show a different ablation efficiency depending on the fluence than the WC-L₂ sample. Furthermore, the two regression lines intersect at that fluences where, according to Table_A 4, the best recovery rates for the respective analytes were determined – for Mo and Eu at approx. 6 J cm⁻².

Now that this has been proven, the question inevitably arises as to whether this phenomenon was also the reason for the insufficient recovery when using the other RMs presented above. To verify this, an analogous fluence-dependent analysis of the WC-L₂ sample was performed using the syn C-S-H₁ RMs. The results are listed in Table_A 6 and Table_A 7 in the appendix. In fact, the same phenomenon can be observed here. Furthermore, an optimal fluence of 6 J cm⁻² could be confirmed. However, the underestimation at < 6 J cm⁻² and the overdetermination at > 6 J cm⁻² are significant more pronounced. In addition, the recovery at the optimal fluence is not as good as that determined with the syn C-S-H₂ RMs. Thus, a matrix effect can still be observed and the syn C-S-H₂ RMs can be considered more suitable for the analysis of WC-L₂ sample.

Now that both the manufacturing process and the laser settings have been optimised, excellent recovery rates (see Table 15 at 6 J cm⁻²) have already been achieved. For the time being, the establishment of an LA-ICP-MS method for quantifying trace elements in C-S-H phases can be considered successful. However, some fine-tuning was now required. The aim was to improve the recovery rates even further to < 5% for all elements. It would also be desirable to either eliminate or specifically compensate for the differences in the dependence of ablation efficiencies (on RM and sample). For this purpose, as briefly mentioned above, the next step was to perform normalisation to one or even both structure-forming elements (Ca and/or Si).

To investigate the effect of normalisation, an analogue analysis of the Mo, Eu, and U concentrations in the WC-L₂ sample was performed using the syn C-S-H₂ RMs at four different fluences (5–8 J cm⁻²); this time, however, ⁴³Ca was also measured. The analyte signals obtained were normalised to the ⁴³Ca signal of the same ablation path. The results are shown in the usual manner in Table 16.

Table 16: Calculated concentrations of Mo, Eu, and U using a normalisation to the ⁴³Ca signals and their deviations from the known value in the WC-L₂ sample (45.9 µg g⁻¹ Mo, 149.9 µg g⁻¹ Eu and 219.2 µg g⁻¹ U) using the syn C-S-H₂ RMs at different laser powers (fluence = 5–8 J cm⁻²), the R² values of the individual calibration curves and the averaged RSD (averaged over the ablation lines, all RMs and all analytes at the respective fluence); 1150 W, [He] (collision gas mode), 0.1 s integration time, 10 Hz, 10 µm s⁻¹, 50 x 50 µm spot size, 1.0 mm ablation lines.

Fluence	C _{Calculated} [µg g ⁻¹]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
5	38.7	106.4	195.0	-15.7	-29.0	-11.1	0.9997	0.9995	0.9994	3.10	2.69
6	39.9	123.9	200.8	-13.0	-17.3	-8.4	0.9999	0.9981	0.9984	5.38	9.58
7	37.1	113.9	196.6	-19.0	-24.0	-10.3	0.9997	0.9979	0.9984	3.52	3.46
8	37.6	114.3	191.8	-18.0	-23.8	-12.5	0.9996	0.9991	0.9993	3.14	2.35

Table 16 clearly shows that normalisation leads to significantly poorer recovery values; severe underestimation can be observed for all fluences. If the same data set is evaluated without such normalisation, the underestimation is significantly smaller; as shown in Table_A 8 in the appendix. For example, at 6 J cm^{-2} the following recoveries are achieved: -5.70% for Mo, -10.09% for Eu, and -0.32% for U. A worse/lower recovery rate when normalising is equivalent to a better ablation efficiency of ^{43}Ca in the sample material (compared to the syn C-S-H_2 RMs). There is no clear reason for this phenomenon. Since nothing similar has been observed so far, it could perhaps be due to errors during the RM production – although this is rather unlikely. Therefore, new RM tablets were prepared. For this purpose, the syn C-S-H_3 RMs were prepared in the manner as shown in Table 6. Here, the matrix material (syn C-S-H) was ground in the PBM (with n-pentane) for one hour prior to the addition of the analytes, with the aim of further improving homogeneity. Furthermore, larger volumes of the analyte solutions were used again and a shorter grinding time of 1 h (in n-pentane) was selected after drying.

Subsequently, analogous to the above, an analysis of the WC-L_2 sample was performed using the syn C-S-H_3 RMs with different fluences ($4\text{--}9 \text{ J cm}^{-2}$). In addition to the C-S-H_3 RMs, a control sample containing $10 \mu\text{g g}^{-1}$ of the same analytes (Mo, Eu, and U) was prepared (syn C-S-H_3 Control) and analysed. During the analysis, the masses ^{30}Si , ^{43}Ca , and ^{44}Ca were measured in addition to the analytes (^{95}Mo , ^{153}Eu , and ^{238}U). The analysis data was then evaluated in the usual manner without normalisation, with normalisation to the summed signals of ^{30}Si and ^{43}Ca , and with normalisation to the summed signals of ^{30}Si and ^{44}Ca . As above, the signals from the same ablation line were used for normalisation. The results obtained are listed in the following tables in the appendix: Table_A 9 (WC-L_2 without normalisation), Table_A 10 (syn C-S-H_3 Control without normalisation), Table_A 11 (WC-L_2 normalisation to $^{30}\text{Si} + ^{43}\text{Ca}$), Table_A 12 (syn C-S-H_3 Control normalisation to $^{30}\text{Si} + ^{43}\text{Ca}$), Table_A 13 (WC-L_2 normalisation to $^{30}\text{Si} + ^{44}\text{Ca}$) and Table_A 14 (syn C-S-H_3 Control normalisation to $^{30}\text{Si} + ^{44}\text{Ca}$). A comparison of Table 15 and Table_A 9 clearly shows that the analyses of the WC-L_2 sample using the syn C-S-H_2 and syn C-S-H_3 RMs do not show any significant difference in recovery rates (deviation values). However, if normalised to the summed signals of ^{30}Si and ^{43}Ca (Table_A 11), this leads to a significant deterioration in the deviation/recovery values. The situation is different when normalised to the summed signals of ^{30}Si and ^{44}Ca (Table_A 13): here, excellent recoveries are achieved for Mo (2.0% deviation at 6 J cm^{-2}) and Eu (-2.2% deviation at 6 J cm^{-2}), whereas U was significantly underestimated with a deviation of -10.6% at 6 J cm^{-2} .

When evaluating the recovery of Mo, Eu, and U in the syn C-S-H_3 Control sample, normalisation to the summed signals of ^{30}Si and ^{44}Ca proves also to be the best method. Looking at Table_A 14, for example, at 6 J cm^{-2} , the deviations for Eu and U are insignificant (-0.1% and -1.5%) and those for Mo are very small (2.2%). In comparison, the deviations of the syn C-S-H_3 Control sample without normalisation are significantly higher (Table_A 10) and are on a similar level to those with normalisation to ^{30}Si and ^{43}Ca (Table_A 12). With that, it can be said that normalisation results in a marginal improvement in recovery, but in the case of C-S-H phases, normalisation to ^{43}Ca should be avoided in the selected measurement mode.

At the end of the chapter, a short summary and outlook:

While developing an LA-ICP-MS method for the quantification of trace elements in C-S-H phases, the most common methods for optimising external calibration have been applied (see Chapter 2.7.3): Matrix-matched standard materials with identical matrices and identical incorporated analytes were produced. Furthermore, the laser power was optimised, and analyses were performed with normalisation to structure-forming elements. All these measures led to excellent recovery for the elements Mo and Eu, whereas U is still severely underestimated (see Table_A 13). This raises the question: Why are very good results achieved for Mo and Eu, but less good ones for U? The exact reasons are difficult to point out but one possibility could be differences in the fractionation index. For example, Fryer et al. [179] found significant differences in the fractionation indices/-factors for Mo, Eu, and U, despite normalisation. Another reason could be the WC-L_2 sample itself. As can be seen in Chapter 3.1.3, the element concentrations of the sample were determined indirectly, i.e., from the supernatant solutions after synthesis [8]. This is common practice (see, for example, Schmeide et al. [140] and Lange et al. [71]), but at this point, quantification using another analytical method (e.g., EXAFS) would be advisable. This would provide certainty as to whether the LA-ICP-MS method really needs further optimisation or whether the U concentration in the WC-L_2 sample was initially determined incorrectly. However, the latter consideration can be considered very unlikely in view of the more than excellent reproducibility of the synthesis (see Figure 1 in article in Chapter 3.1.3 [8]) and the very good recovery of Mo and Eu. If, for example, a systematic error had been made in the analysis of the supernatant solution (after synthesis of the WC-L_2 sample), the quantification of Mo and Eu would also have been incorrect. Since this is not the case, the origin of the less precise U recovery is most likely to be found in different fractionation indices/-factors.

To put this result into perspective, one must look at the literature. Although the aim here was to achieve deviations of < 5%, in literature deviations of up to 10% are considered acceptable, if not good [75, 168, 170]. Based on this standard, the LA-ICP-QQQ method developed here can be considered successful.

3.2.1.2 External SAM LA-ICP-QQQ for fast quantification of elemental ratios

Chapter 3.2.1.1 already presented the successful development of an LA-ICP-QQQ method using external calibration. However, as shown in Chapter 2.7.3, there are other approaches besides external calibration for reliably quantifying trace elements in solid phases. One very promising approach is the “dual sample/standard approach” according to O'Connor et al. [168], which presented a method for solution-based calibration. Although the production of external RMs offers many advantages for routine measurements, it is rather impractical in the case of frequently changing matrices. An adaptation of the “dual sample/standard approach” promises to remedy this problem. However, to successfully implement this method, the experimental setup, and thus the coupling technique, must first be developed. In the case of O'Connor et al. [168], the ablated aerosol from the laser ablation was combined with the aerosol from the spray chamber of the ICP-MS via a Y-piece. Fortunately, the coupling is way easier to achieve when using an Agilent 8900 ICP-QQQ with integrated HMI (high matrix introduction) – quite similar to Bolea-Fernandez et al. [187]. The setup is shown schematically in Figure 33.

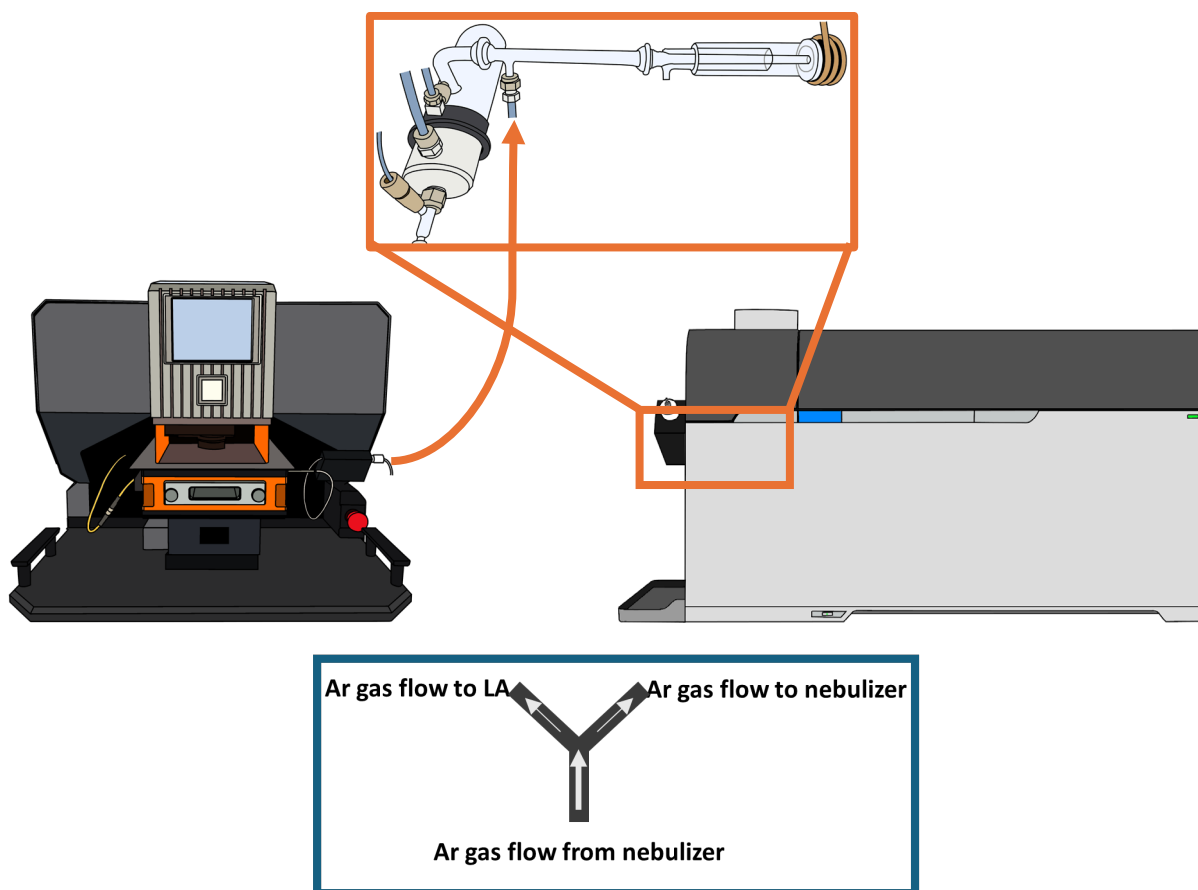


Figure 33: Schematic Drawing of the setup for external SAM LA-ICP-QQQ quantification technique (dual sample/standard approach) with an ESI NRW213 laser ablation and an Agilent 8900 ICP-QQQ with HMI (high matrix introduction).

Figure 33 shows the key coupling steps when performing an LA-ICP-QQQ analysis using the dual sample/standard approach; hereinafter referred to as external SAM (standard addition method). In this method, the Ar gas flow at the nebuliser gas inlet of the ICP-QQQ device is routed through a Y-piece (blue box in Figure 33). As briefly described in Chapter 3.2.1.1, Ar gas is required at the LA primarily to accelerate aerosol transport. Ar gas is also required as a nebulisation gas at the ICP-QQQ. Both devices are supplied with sufficient Ar gas via the Y-piece. Again, He was used as the cell gas for the LA in all subsequent experiments at a flow rate of 800 mL min⁻¹. The ablated material is then transported via the gas stream (He + Ar) to the sample intake unit of the ICP-QQQ and mixed with the liquid-aerosol there via the HMI (orange box in Figure 33). The liquid aerosol was formed in the usual manner via the nebuliser and the double-pass spray chamber (also shown in the orange box in Figure 33). All experiments were conducted in wet and therefore hot plasma (1550 W) with an integration time of 0.1 s and a nebuliser gas flow of 1.1 L min⁻¹.

A brief note at this point: On the software side – MassHunter (Version 5.2 D.01.02) and ActiveView 2 (Version 1.5.0.25) – it was not possible to operate the LA and the autosampler (Agilent SPS4, Santa Clara, USA) as sample tasks at the same time. Therefore, the analysis had to be performed manually, using the following sequence:

First, the autosampler needle was moved into the corresponding solution. As soon as a stable signal was observed in the MassHunter tune monitor window, the signal monitor was restarted, or the signals were reset with “Clear Plot.” The signal was then recorded over the period defined for the monitor window (acquisition time of 165 s). After this period, the signal was fixed by pressing the “Stop Signal Monitor” button. The desired measurement results can then be read (usually “Avg. Counts” and RSD). The same procedure applies to ablation: First, the signal from the solution must be stable, then ablation is started, and as soon as a stable signal is measured from the solution and ablation, the measurement window is started with “Clear Plot.”

For an initial proof of concept of the proposed coupling technique, a simple calibration curve for Eu in Calcigel was to be created. For this purpose, similar to Chapter 3.2.1.1, a Calcigel pellet spiked with Eu was prepared in advance: 1.0 g of Calcigel was mixed with 1 mL of a 100 mg L⁻¹ Eu solution in a mortar, then dried overnight (at 110°C) and finally pressed at 4 t for 30 min (stamp Ø = 10 mm). The target concentration of Eu in the solid was therefore 100 µg g⁻¹. The aim was now to establish an adequate calibration curve using the external SAM. For the calibration from solution, acidic solutions (approx. 2% HNO₃) containing 10 µg L⁻¹ Sc and Ho as well as Eu in the concentrations specified in Table 17 were prepared. The manufactures information of the samples used are listed in Table_A 15.

The proof of concept described yielded the measured values shown in Table 17. The RSD values are deliberately not shown, as they are not relevant here. Suffice it to say that the RSD of Eu indicated significant inhomogeneity, as expected due to the simple homogenisation in the mortar. Based on the values listed in Table 17, the Eu signals were normalised to the Ho ones and the calibration curves shown in Figure 34 were then plotted.

Table 17: Measurement signals of Sc, Eu, and Ho during external SAM analysis of spiked Calcigel pellet ($100 \mu\text{g g}^{-1}$ Eu); nebuliser gas flow 1.1 L min^{-1} , 1550 W, [NoGas]-mode, 0.1 s integration time, 10 Hz, $10 \mu\text{m s}^{-1}$, $50 \mu\text{m}$ $\varnothing$ spot size, data acquisition time 165 s.

Solution	Ablation of Calcigel	Eu [$10^6 \cdot \text{CPS}$]	Sc [$10^3 \cdot \text{CPS}$]	Ho [$10^3 \cdot \text{CPS}$]
Blank	Yes	1.28	600	700
Blank	No	--	400	700
$50 \mu\text{g L}^{-1}$	Yes	3.28	510	710
$50 \mu\text{g L}^{-1}$	No	1.86	375	700
$100 \mu\text{g L}^{-1}$	Yes	5.22	510	710
$100 \mu\text{g L}^{-1}$	No	3.70	355	690
$200 \mu\text{g L}^{-1}$	Yes	9.30	495	705
$200 \mu\text{g L}^{-1}$	No	7.29	360	695

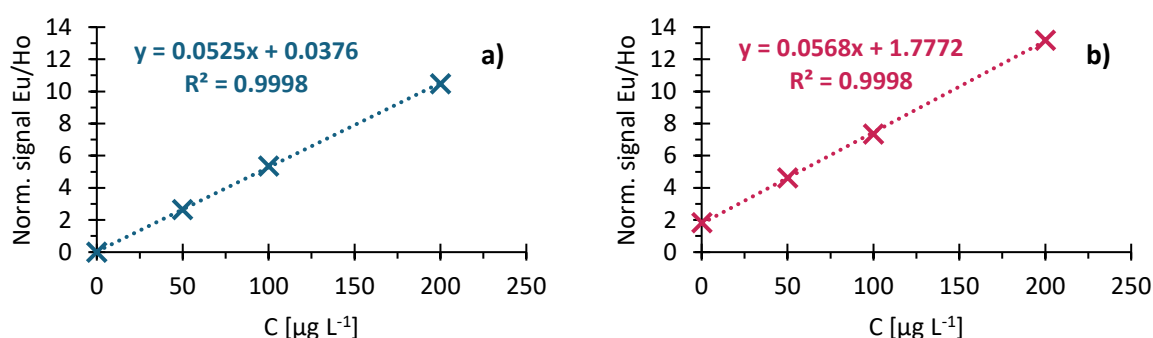


Figure 34: Calibration curves for Eu, based on the values shown in Table 17; a) Calibration from solution; b) Calibration from solution while ablating; measurement conditions see Table 17.

Above all, the R^2 values of the calibration curves in Figure 34 show that the nebuliser performance is sufficient and that the coupling technique shown in Figure 33 leads to valid measurement results.

Before attempting to reproduce the results by O'Connor et al. [168], the basic theory should be described first:

When performing calibration from solution, Equation 10 generally applies, whereby the intensity (I) [counts s^{-1}] (counts per second; CPS) is calculated from the mass flow rate ($\dot{m}_A$) [g s^{-1}], the concentration (C_A) [g g^{-1}], and the sensitivity/slope (S_A) [counts g^{-1}]. The subscript "A" indicates that these are variables resulting from the analyte [168].

$$I = \dot{m}_A \cdot C_A \cdot S_A \quad (10)$$

If now the fact, that signals can arise from both, the solution and the ablated solid material, is considered, Equation 11 can be drawn. The superscript notation “L” represents the respective variables arising from the solution, and the superscript “S” represents the variables arising from the solid material. Figure 35 illustrates this principle: the calibration curve from the solution (Equation 10) is shown in blue, and the calibration curve from the solution with simultaneous ablation of the sample material (Equation 11) is shown in red [168].

$$I = \dot{m}_A^L \cdot S_A^L \cdot C_A^L + \dot{m}_A^S \cdot S_A^{S+L} \cdot C_A^S \quad (11)$$

A small note at this point: According to O'Connor et al. [168], the slopes (sensitivities) are an excellent indicator of matrix effects. Parallel slopes indicate no mutual matrix effects.

To obtain the concentration of the analyte in the solid sample (C_A^S), according to O'Connor et al. [168], I must be set to 0 and Equation 11 must be rearranged according to C_A^S . This results in Equation 12, where $C_{A/0}^L$ corresponds to the x-axis intercept (see Figure 35).

$$C_A^S = -\frac{\dot{m}_A^L}{\dot{m}_A^S} \cdot \frac{S_A^L}{S_A^{S+L}} \cdot C_{A/0}^L \quad (12)$$

Based on Equation 12, the analyte concentration in the solid can now be calculated. $C_{A/0}^L$, S_A^L , and S_A^{S+L} can all be taken from the graphs in Figure 35. Only the mass flow ratios ($\frac{\dot{m}_A^L}{\dot{m}_A^S}$) are still unknown. However, adding an IS (subscript “I”) to the solid and the solution can remedy this. If the concentration of the IS is known, the mass flow ratio of the IS ($\frac{\dot{m}_I^L}{\dot{m}_I^S}$) can be calculated using Equation 13 [168].

$$-\frac{\dot{m}_I^L}{\dot{m}_I^S} = \frac{C_I^S}{\frac{S_I^L}{S_I^{S+L}} \cdot C_{I/0}^L} \quad (13)$$

At this point, the assumption that the mass flow ratios are the same for all elements in the solid comes into play (Equation 14). Once the concentration of one element in the solid is known (in that case the one of the IS), the mass flow ratio can be calculated and applied to all other elements/analytes [168].

$$\frac{\dot{m}_I^L}{\dot{m}_I^S} = \frac{\dot{m}_A^L}{\dot{m}_A^S} \quad (14)$$

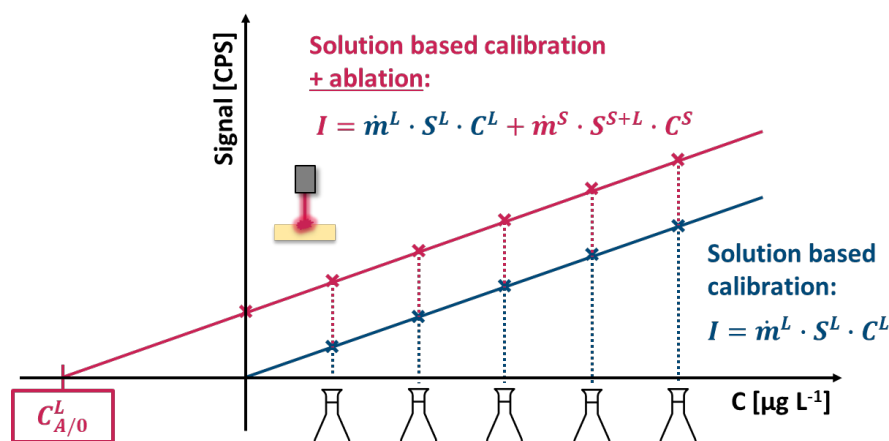


Figure 35: Calibration principle of the external SAM after the dual sample/standard approach after O'Connor et al. [168]; illustration also adapted from O'Connor et al. [168].

The aim was now to apply or adapt the theoretical principles described above. Therefore, similar to O'Connor et al. [168], Ti, Co, Cu, Tl, and U in a NIST® SRM® 612 standard (Standard Reference Material® 612, trace elements in glass, National Institute of Standards and Technology, Gaithersburg, USA) were analysed. During this, acidic solutions (approx. 2% HNO₃) were prepared containing the analytes above in concentrations of 0.5, 1, 5, 10, 20, 50, and 100 μg L⁻¹. In addition to the analytes, each solution contains 10 μg L⁻¹ Sc and Ho. The manufacture information of the solutions used are listed in Table_A 15. Subsequently, both the solutions and the NIST® 612 standard were analysed in the manner described above. All analytes were measured (quasi-) simultaneously for each solution/ablation line. During data evaluation, the signals from Ti, Co, and Cu were normalised to those from Sc, and the signals from Tl and U were normalised to those from Ho. Subsequently, a background correction was performed by defining the respective signals of a blank solution. This form of data processing was also performed in all subsequent analyses.

Figure 36 shows the calibration curves (analogous to Figure 35) of U resulting from the analysis of the NIST® 612 standard. Figure 36 a) shows the calibration curve from the solution (L) and from the solution with simultaneous ablation (S+L) without any normalisation. In contrast, Figure 36 b) shows the same calibration but with normalised signals. It is clear that without normalisation, the calibration curves of L and S+L, as described by O'Connor et al. [168] (see above), do indeed run. Thus, no matrix effects can be observed. In the case of normalisation (Figure 36 b)), however, the calibration curves intersect. The reason for this is simple: both Sc and Ho are also contained in NIST® 612, which is why the signal of these elements increases during simultaneous ablation, leading to flatten the calibration curve. As will be shown later (in Table 20), this circumstance does not detract from the analysis but rather improves the result marginally. This is because it not only compensates for device fluctuations from the solution (e.g., nebuliser performance), but also during ablation and aerosol transport.

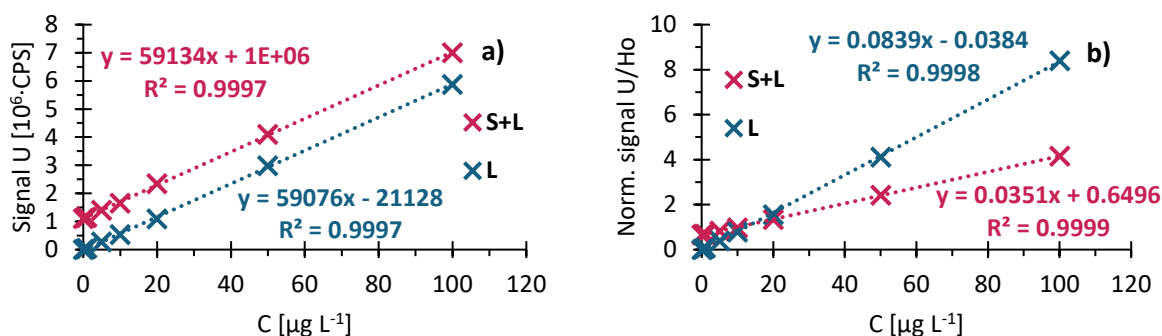


Figure 36: Calibration curves of the external SAM of U in NIST® 612; a) without normalisation and b) with normalisation on Ho signals; with L = calibration curve from solution and S+L = calibration curve from solution while ablating; nebuliser gas flow 1.1 L min^{-1} , 1550 W , [NoGas]-mode, 0.1 s integration time, 8 J cm^{-2} , 10 Hz , $10 \mu\text{m s}^{-1}$, $50 \mu\text{m}$ $\varnothing$ spot size, data acquisition time 165 s .

The parameters listed in Table 18 are derived from the analysis of the NIST® 612 standard shown in Figure 36. Since the concentrations of all analytes in the NIST® SRM® 612 are known ($C_{A/NIST}^L$), the mass flow ratios ($\frac{\dot{m}_A^L}{\dot{m}_S^L}$) can also be calculated. As described above, it is assumed that these should be (approximately) the same for all analytes. A glance at the values in Table 18 shows that this is indeed the case, with one exception. The mass flow ratio of Cu deviates significantly from the other analytes. The reason for this is not clear at this point, but this phenomenon can also be observed without normalisation or background correction (see Table_A 16, Table_A 17 and Table_A 18 in the appendix).

Table 18: Parameters/variables obtained from the underground corrected and normalised external SAM analysis of the NIST® 612 standard material, where $C_{A/NIST}^S$ = known concentration of the analyte in the NIST® Standard; measurement conditions see Figure 36.

Element	$C_{A/0}^L [\mu\text{g L}^{-1}]$	$S_A^L [\text{CPS L } \mu\text{g}^{-1}]$	$S_A^{S+L} [\text{CPS L } \mu\text{g}^{-1}]$	$\frac{\dot{m}_A^L}{\dot{m}_S^L}$	$C_{A/NIST}^S [\mu\text{g kg}^{-1}]$
Ti	-22.804	0.00510	0.00204	879.28	50,100
Co	-17.669	0.09474	0.03816	809.28	35,500
Cu	-21.066	0.05043	0.02037	723.05	37,700
Tl	-7.616	0.06648	0.02665	826.29	15,700
U	-18.521	0.08392	0.03508	843.60	37,380

Now that it has been proven that the mass flow ratios are indeed all approximately identical, the concentrations of the analytes can be calculated using Equation 12. Since every analyte has its own mass flow ratio, the aim is to test how the recovery rates of the individual analytes behave when different analytes act as the internal standard. Therefore, the mass flow ratio of the defined IS was used to calculate the concentrations of all other analytes. For the case of the underground corrected and normalised data (Table 18), the calculated analyte concentrations in the NIST® 612 material ($C_{A/Calc}^S$) and the resulting deviations (Δ in [%]) from the known concentration values are shown in Table 19. For

the other cases, depending on if an underground correction or a normalisation was applied, the resulting concentrations and deviations are shown in Table_A 19, Table_A 20 and Table_A 21 (appendix).

Table 19: Calculated concentrations in the NIST® 612 ($C_{A/calc}^S$) using Equation 12 and the values listed in Table 18 (with underground correction and normalisation); for each mass flow ratio listed there, the resulting concentrations and the absolute deviation (Δ) were calculated for all analytes (the certified values ($C_{A/NIST}^S$) are also shown in Table 18).

Element	Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of	
	Ti		Co		Cu		Ti		U	
	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]
Ti	50100	0.0	46112	8.0	41198	17.8	47080	6.0	48067	4.1
Co	38571	8.7	35500	0.0	31717	10.7	36246	2.1	37005	4.2
Cu	45846	21.6	42196	11.9	37700	0.0	43083	14.3	43985	16.7
Ti	16707	6.4	15377	2.1	13738	12.5	15700	0.0	16029	2.1
U	38961	4.2	35860	4.1	32039	14.3	36613	2.1	37380	0.0

As already mentioned in Chapter 3.2.1.1, deviations in recovery values of < 10% are generally considered good if not very good. As can be seen from Table 19, Table_A 19, Table_A 20 and Table_A 21, such recoveries have been achieved for all analytes, except Cu. The significant deviation in the case of Cu is, as already mentioned, due to the significantly different mass flow ratio. To quantify the quality of the analytical method and thus also evaluate the approach of background correction and normalisation, the deviations listed in Table 19, Table_A 19, Table_A 20 and Table_A 21 are averaged for each mass flow ratio used. However, since Cu, for reasons unknown, does not fit into the picture (deviations > 10%), it is advisable to exclude Cu from this calculation and average the deviations without the values for and based on Cu. The resulting averaged absolute deviations are shown in Table 20.

Table 20: Averaged deviations from Table 19, Table_A 19, Table_A 20 and Table_A 21; the averaged values were calculated for each mass flow ratio and always excluding the values for and based on Cu; e.g., the first value of Ti (column 1 and row 1) was averaged from the values 8.65, 6.41, and 4.23 in first column in Table 19; a $\Delta = 0.0\%$ is always excluded since it would distort the results.

Elements which $\dot{m}_A^L/\dot{m}_A^S$ used for the calculation of $C_{A/calc}^S$	Avg. Δ [%]			
	Underground correction		No Underground correction	
	Normalisation	No normalisation	Normalisation	No normalisation
Ti	6.4 $\pm$ 2.2	5.1 $\pm$ 3.2	6.4 $\pm$ 2.2	5.2 $\pm$ 2.9
Co	4.7 $\pm$ 3.0	9.8 $\pm$ 2.2	4.6 $\pm$ 2.8	9.8 $\pm$ 2.4
Cu	–	–	–	–
Ti	3.4 $\pm$ 2.3	5.2 $\pm$ 4.7	3.3 $\pm$ 2.1	5.3 $\pm$ 4.6
U	3.5 $\pm$ 1.2	7.3 $\pm$ 5.8	3.4 $\pm$ 1.1	7.5 $\pm$ 5.7

The averaged deviations listed in Table 20 clearly confirm the excellent recovery of the analytes, indicating that the external SAM, and thus the dual sample/standard approach according to O'Connor et al. [168], was successfully implemented. Furthermore, it can be concluded from the average absolute deviations in Table 20 that, on the one hand, normalisation leads to a significant improvement in recovery, but that background correction has no significant effect. This proves that normalisation to an IS leads to a significant improvement in the analysis. Although background correction had no positive effect on the result here, it will nevertheless be performed in the following analyses, as this allows any matrix effects and instrument contamination to be ruled out from the outcome.

During the data analysis of the external SAM analysis of the NIST® 612 standard described above, some very interesting empirical observations were made, which will enable a adaption of the external SAM in the future. These observations relate to the sensitivity from the solution (S^L) and the sensitivity during simultaneous ablation (S^{S+L}). Table 18, Table_A 16, Table_A 17 and Table_A 18 show that for two different analytes (A1 and A2) the following applies:

$$\frac{S_{A1}^L}{S_{A1}^{S+L}} \approx \frac{S_{A2}^L}{S_{A2}^{S+L}} \quad (15)$$

In the case without normalisation, with parallel calibration curves, Equation 15 translates to Equation 16.

$$\frac{S_A^L}{S_A^{S+L}} \approx 1 \quad (16)$$

If Equation 16 is now inserted into Equation 12, Equation 17 is obtained.

$$-\frac{\dot{m}_A^L}{\dot{m}_A^S} = \frac{C_A^S}{C_{A/0}^L} \quad (17)$$

Since, as already mentioned and proven several times, the mass flow ratios of different analytes contained in the solid are approximately the same (see, for example, Table 18), Equation 14 can be reformulated as Equation 18 (for A1 and A2).

$$\frac{\dot{m}_{A1}^L}{\dot{m}_{A1}^S} \approx \frac{\dot{m}_{A2}^L}{\dot{m}_{A2}^S} \quad (18)$$

With that, the Equations 17 and 18 thus result in the correlation shown in Equation 19.1. Rearranging this equation yields Equation 19.2.

$$\frac{C_{A1}^S}{C_{A1/0}^L} \approx \frac{C_{A2}^S}{C_{A2/0}^L} \quad (19.1)$$

$$\frac{C_{A1}^S}{C_{A2}^S} \approx \frac{C_{A1/0}^L}{C_{A2/0}^L} \quad (19.2)$$

In other words, Equation 19.2 means that the ratio of two elements/analytes in the solid must be equal to the ratio of the corresponding x-axis sections. If this hypothesis is correct, it would be possible to quantify elemental ratios very quickly using LA-ICP-MS/-QQQ analysis without adding any IS. All that would be required is to follow the external SAM approach described above: calibration from the solution with simultaneous ablation.

To test the hypothesis set out in Equation 19.2, the data from the NIST® 612 analysis, described above, is used again. Since all element contents for Ti, Co, Cu, Tl, and U are certified ($C_{A/NIST}^S$ in Table 18), the respective ratios are also known (see Table 21). In the case of background-corrected and normalised data evaluation, the elemental ratios shown in Table 22 result from the x-axis sections ($C_{A/0}^L$) listed in Table 18. The deviations from the certified ratios can then be calculated (Table 23).

Table 21: Certified elemental ratios in the NIST® 612 standard; calculated from $C_{A/NIST}^S$ in Table 18.

X/X	Ti	Co	Cu	Tl	U
Ti	--	0.71	0.75	0.31	0.75
Co	1.41	--	1.06	0.44	1.05
Cu	1.33	0.94	--	0.42	0.99
Tl	3.19	2.26	2.40	--	2.38
U	1.34	0.95	1.01	0.42	--

Table 22: Elemental ratios in NIST® 612 standard calculated using Equation 19.2 and the $C_{A/0}^L$ values listed in Table 18.

X/X	Ti	Co	Cu	Tl	U
Ti	--	0.77	0.92	0.33	0.81
Co	1.29	--	1.19	0.43	1.05
Cu	1.08	0.84	--	0.36	0.88
Tl	2.99	2.32	2.77	--	2.43
U	1.23	0.95	1.14	0.41	--

Table 23: Deviation of the calculated elemental ratios using Equation 19.2 (Table 22) from the certified ratios in Table 21.

Deviation of the ratios [%]					
X/X	Ti	Co	Cu	Tl	U
Ti	–	8.55	18.55	6.17	8.13
Co	9.35	–	10.93	2.60	0.45
Cu	22.77	12.27	–	15.19	12.78
Tl	6.58	2.53	13.19	–	2.09
U	8.86	0.45	11.33	2.14	–

The deviations listed in Table 23 show, once again, that all analytes (except Cu) are in a good to very good agreement with the certified values (deviation < 10%). If these are now averaged, excluding those for Cu (for known reasons), the result is an average absolute deviation of $5 \pm 3\%$. Thus, using the example of the NIST® 612 analysis, it is proven that the hypothesis set out in Equation 19.2 is indeed valid.

So far, it has been proven that the coupling technique shown in Figure 33 leads to valid measurement results when performing an external SAM and enables the quantification of trace elements in solid phases using internal standards. Furthermore, a new variation of the external SAM has been established, enabling the rapid quantification of elemental ratios in solids without the addition of internal standards. Accordingly, the next step would be to apply these methods to the issues of repository research. However, as Chapter 3.2.1.1 has demonstrated in detail, a valid LA-ICP-QQQ method for quantifying trace elements in C-S-H phases has already been developed, so it would be advisable to adapt the method for quantifying element ratios in C-S-H phases. Since, as has also been described several times, the C/S ratio is one of the most important factors in chemical questions relating to C-S-H phases, a quick and simple method for quantifying this is a powerful tool. Therefore, this will be done in the following.

Due to its commercial availability, Circosil® was used as the analysed material. Similar to the C-S-H samples in Chapter 3.2.1.1, it was ground in a mortar and pressed into a pellet with 4 t for 30 min (stamp $\varnothing = 10$ mm). Subsequently, acidified calibration solutions (approx. 2% HNO₃), each containing 10 $\mu\text{g L}^{-1}$ Sc and Ho, were prepared with Si and Ca concentrations of 0, 0.5, 1, 5, 25, 75, and 150 mg L⁻¹. The relevant manufacturer's information for the chemicals used can be found again in Table_A 15. Both the solutions and the solid sample were measured according to the procedure described above. However, it should be noted that since the main elements of the solid were analysed instead of trace elements, the measurement signals would far exceed the recommended range of the ICP-QQQ device. Therefore, it had to be deliberately “poorly tuned,” i.e., the measurement signals had to be reduced. To do so, the flow rate of the cell gas (H₂) was increased to 5.8 mL min⁻¹ and the laser power was reduced (fluence = 2 J cm⁻²). Furthermore, especially in the case of Ca, it was necessary to switch to the less abundant isotope ⁴⁴Ca. Thus, on-mass was measured in [H2]-mode with the mass pairs (Q1; Q2) Si (28; 28), Ca (44; 44), Sc (45; 45) and Ho (165; 165).

During the external SAM analysis of Circosil[®], it was determined that Sc is contained in Circosil[®] itself, and unfortunately in an extremely inhomogeneous manner. This resulted in RSD values of the ⁴⁵Sc signal of approx. 100% during ablation; in comparison to an RSD of approx. 3.5% for ⁴⁴Ca. Thus, ⁴⁵Sc was unsuitable as an IS, and the ²⁸Si and ⁴⁴Ca signals were normalised to those of ¹⁶⁵Ho. The resulting (underground corrected and normalised) calibration curves are shown in Figure 37. The non-normalised calibration curves are shown in Figure_A 1 in the appendix.

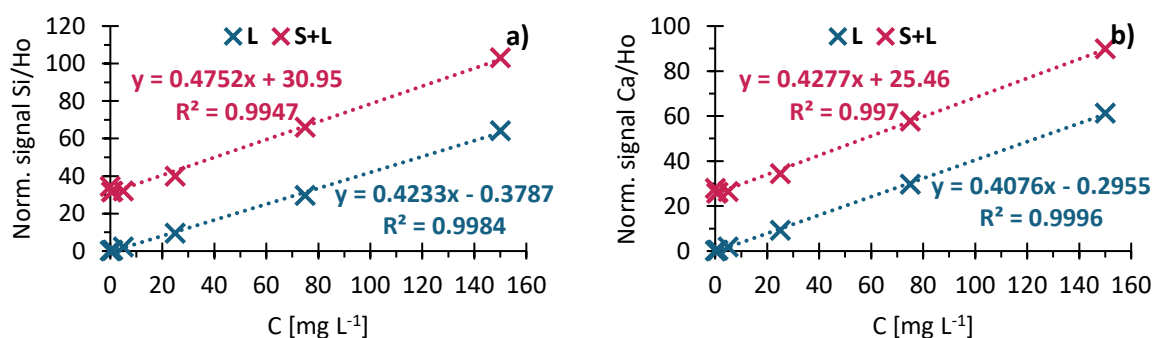


Figure 37: Calibration curves of a) ²⁸Si and b) ⁴⁴Ca (both underground corrected and normalised on ¹⁶⁵Ho signal) from external SAM of Circosil[®]; with L = calibration curve from solution (concentration 0, 0.5, 1, 5, 25, 75, and 150 mg L⁻¹) and S+L = calibration curve from solution while ablating; nebuliser gas flow 1.1 L min⁻¹, 1550 W, [H₂]-mode (5.8 mL min⁻¹), 0.1 s integration time, 2 J cm⁻², 10 Hz, 10 μm s⁻¹, 50 μm Ø spot size, data acquisition time 165 s.

The calibration curves in Figure 37 and Figure_A 1 run almost perfectly parallel for each analyte, which indicates that there are no matrix effects or similar issues to consider. Thus, now, similar to the analysis of the NIST[®] SRM[®] 612, the values for $C_{A/0}^L$, S_A^L , and S_A^{S+L} for Si and Ca can be taken or calculated from those calibration curves. These are listed in Table 24, both for normalisation to Ho and without any normalisation. Based on those values and using Equation 19.2, the Ca/Si mass ratio and molar ratio can be calculated (see Table 25).

Table 24: Parameters/variables obtained from the underground corrected, normalised and not normalised external SAM analysis of Circosil[®]; measurement conditions see Figure 37 and Figure_A 1.

Element	Normalised			Not normalised		
	$C_{A/0}^L$ [μg L ⁻¹]	S_A^L [CPS L μg ⁻¹]	S_A^{S+L} [CPS L μg ⁻¹]	$C_{A/0}^L$ [μg L ⁻¹]	S_A^L [CPS L μg ⁻¹]	S_A^{S+L} [CPS L μg ⁻¹]
Si	-65.14	0.4233	0.4752	-83.10	131,837	137,679
Ca	-59.52	0.4076	0.4277	-75.39	127,024	124,925

Table 25: Ca to Si mass and molar ratios resulting from the external SAM of Circosil® described in Figure 37 and Figure_A 1; the ratios for the normalised and not normalised data set where calculated using values shown in Table 24 and Equation 19.2.

	Ca/Si <u>mass</u> ratio	Ca/Si <u>molar</u> ratio
Normalised	0.914	0.640
Not normalised	0.907	0.636

Table 25 shows that in the case of the external SAM analysis of Circosil®, it makes no significant difference whether the measurement signals are normalised or not; both are very close together (C/S of 0.640 and 0.636). However, to be able to evaluate this analysis result definitively, it must be compared or validated with results from other analytical methods. For this purpose, the manufacturer's XRF data is used first. This yields the following mass fractions: 55.5% SiO₂ and 35.5% CaO [108]. From these values, a C/S ratio of 0.647 can be calculated. This is just 1.1% higher than the one determined using the external SAM LA-ICP-QQQ method (in the normalised case). Another comparative value is provided by an energy dispersive X-ray spectroscopy (EDX) analysis conducted by former members of the working group (commissioned by Dr. Kristina Brix and carried out by Dr. Mana Mohamed). This resulted in a C/S ratio of 0.68 ± 0.04 , which is only 5.9% above the value determined here (also for the normalised case). This proves once again that the newly developed variation of the external SAM provides valid measurement results, regardless of the sample material.

At this point, a brief summary and outlook:

An LA-ICP-QQQ coupling method was developed to implement the dual sample/standard approach according to O'Connor et al. [168]. Besides the LA and the ICP-QQQ devices, the coupling method presented here requires only one other commercially available component: the Y-piece. Using this technique, the dual sample/standard approach was applied to the quantification of Ti, Co, Cu, Tl, and U in a NIST® 612 standard, resulted in deviations of < 10% for the analytes Ti, Co, Tl, and U, and in many cases even < 5%. It can therefore be concluded that the adaptation of the dual sample/standard approach according to O'Connor et al. [168], using the selected coupling technique here referred as external SAM, was successful.

In addition to the adaption of existing method to a new system, O'Connor's approach, and thus the external SAM method, was further developed to enable rapid quantification of element ratios in solid material. To achieve that it was only required prior to analysis to prepare calibration solutions and in the case of powder samples, these must also be pressed into tablets. This differs from the dual sample/standard approach according to O'Connor et al. [168], where an IS had to be used. This further development was applied to the NIST® 612 standard and to the C-S-H phase Circosil®. In the case of the NIST® 612 standard different M_1/M_2 ratios ($M_1, M_2 = \text{Ti, Co, Cu, Tl, U}$) were determined using the same data set as for the quantification before. For the analytes Ti, Co, Tl and U again deviation from the certified ratios of < 10% could have been achieved. For Circosil® the results were even better. Compared to the results determined using RFA and EDX analysis, deviations of the C/S ratio of 1.1% and 3.1% could have been achieved. This has enabled the establishment of a new stage in the development of external SAM, which allows simple, fast, commercially accessible, and valid determination of element ratios in solid phases using LA-ICP-MS.

Excuse:

To further underscore the versatility and easy accessibility of the external SAM, another application case, apart from repository research, will now be briefly presented. Here, the Co/Fe ratio in $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles – synthesis by Kimia Moghaddari (member of the working group) after Moghaddari et al. [188] – was quantified and compared with other analytical methods. For this purpose, dried nanoparticles were pressed at 4 t for 1 h (stamp $\varnothing = 10$ mm) and acidic calibration solutions (approx. 2% HNO_3) were prepared in Fe and Co concentrations of 0, 0.005, 0.1, 0.5, 2, and 10 mg L^{-1} , which also contained 10 $\mu\text{g L}^{-1}$ Sc, Y, and Ho. The relevant manufacturer's information for the chemicals used can be found again in Table_A 15. Since the main elements of the solid were also examined in this case, the smallest possible fluence (for a given spot size) was selected (1.04 J cm^{-2}). Furthermore, the analytes were measured in [He] collision gas mode with an increased He flow rate of 6.0 mL min^{-1} .

The underground corrected and normalised calibration curves obtained from the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ analysis are shown in Figure 38 and the resulting variables for calculating the Co/Fe ratio are listed in Table 26. The corresponding analogues for the non-normalised case can be found in Figure_A 2 and Table_A 22.

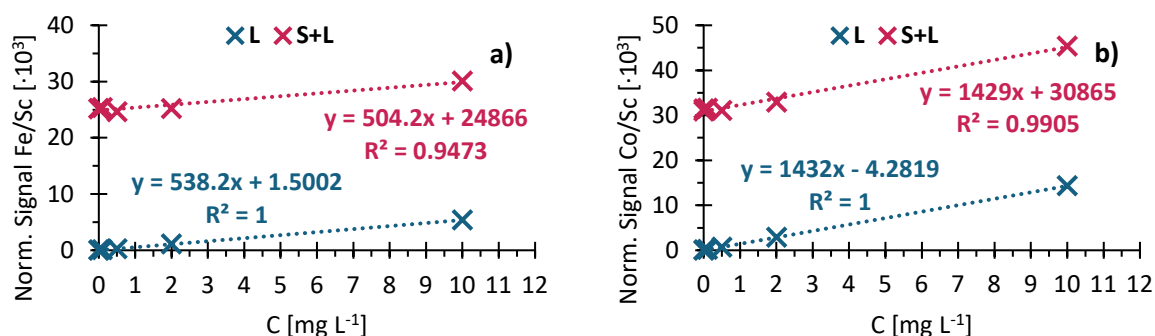


Figure 38: Calibration curves of a) ^{56}Fe and b) ^{59}Co (both normalised on ^{45}Sc signal) from external SAM of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$; with L = calibration curve from solution (concentration 0, 0.005, 0.1, 0.5, 2 and 10 mg L^{-1}) and S+L = calibration curve from solution while ablating; nebuliser gas flow 1.1 L min^{-1} , 1550 W, [He]-mode (6.0 mL min^{-1}), 0.1 s integration time, 1.04 J cm^{-2} , 10 Hz, $10 \mu\text{m s}^{-1}$, $30 \mu\text{m}$ $\varnothing$ spot size, $600 \mu\text{m}$ ablation lines.

Table 26: Parameters/variables obtained from the underground corrected and normalised external SAM analysis of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$; measurement conditions see Figure 38.

Element	$C_{A/0}^L$ [$\mu\text{g L}^{-1}$]	S_A^L [CPS L μg^{-1}]	S_A^{S+L} [CPS L μg^{-1}]
Fe	-49.321	538.2	504.17
Co	-21.595	1,431.5	1,429.29

As above, the values in Table 26 and Table_A 22 can now be used to calculate the corresponding mass and molar ratios using equation 19.2. These are listed in Table 27 for both the normalised and non-normalised data evaluation. Unlike the NIST® SRM® 612 analysis, there is only a small difference between the normalised and non-normalised data. The reasons for this cannot be determined at this

point. In general, however, when looking at Figure 38 and Figure_A 2, it is noticeable that the R^2 values of the S+L curves are marginally better in the non-normalised case. This does not necessarily mean that the results are more valid, but it can be a useful indication.

Table 27: Co/Fe mass and molar ratios resulting from the external SAM of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ described in Figure 38; the ratios for the normalised and not normalised data set where calculated using Equation 19.2 and the values shown in Table 26 and Table_A 22.

	Co/Fe <u>mass</u> ratio	Co/Fe <u>molar</u> ratio	x in $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$
Normalised	0.438	0.415	0.88
Not normalised	0.468	0.443	0.92

To ultimately provide clarity, the results in Table 27 are compared with those from other analytical methods. The measurement data from an ICP-QQQ and an EDX analysis were used for this purpose. These analyses were performed by Kimia Moghaddari (member of the working group) and analogously to those described in Moghaddari et al. [188] (but not the same materials). The molar Co/Fe ratios of all analytical methods are listed in Table 28.

Table 28: Comparison of the Co/Fe molar ratio and x in $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ for different analytical methods; for the LA-ICP-QQQ results the following counts: “normalised / not normalised”.

	LA-ICP-QQQ		ICP-QQQ		EDX	
	Co/Fe <u>molar</u> ratio	x	Co/Fe <u>molar</u> ratio	x	Co/Fe <u>molar</u> ratio	x
$\text{Co}_x\text{Fe}_{3-x}\text{O}_4$	0.415 / 0.443	0.88 / 0.92	0.417	0.88	0.449	0.93

A comparison of the results of the Co/Fe ratio from the external SAM LA-ICP-QQQ, the solution-based ICP-QQQ, and the EDX analysis show that the values diverge only by a maximum of 7.6% (see Table 28). However, this is not due to the inaccuracy of the external SAM, but rather to the fact that the established methods using ICP-QQQ and EDX already diverge by 7.1%. Interestingly, the values from the normalised external SAM and those from the ICP-QQQ analysis match extremely well (Co/Fe = 0.415 and 0.417; 0.5% deviation), while the same applies to the values from the non-normalised external SAM and the EDX analysis (Co/Fe = 0.443 and 0.449; 1.3% deviation). Overall, it can therefore be said that all results from all analytical methods match excellently. However, the question remains: Which value is the most accurate? In general, a solution-based ICP-QQQ analysis can be considered the most accurate of the methods listed in Table 28. Since the external SAM analysis of the NIST® 612 standard has shown that normalisation leads to better results, the agreement of the results from normalised external SAM and ICP-QQQ can be considered as confirmation of the corresponding values. This would prove once again that the newly developed variation of external SAM allows a rapid quantification of elemental ratios and provides valid and extremely reliable results.

4. Conclusion and Outlook

The aim of this work was to close gaps in knowledge regarding retention and remobilisation mechanics of repository-relevant elements on construction and backfill materials as well relevant for this usage. Furthermore, the analytical methodology catalogue was to be expanded so that experiments that contribute to a safety assessment for a future repository could be conducted more efficiently and with greater gain of knowledge.

In a first study, the retention behaviour of the elements Cs, Sm, Eu and U was investigated on commercially available C-S-H phases. This study presents the first results of time-dependent retention experiments in which the analytes in the nanomolar concentration range were combined in a mixture (waste cocktail = WC; with a total of 8 elements) in an alkaline and partly highly saline background solution. All in all, it was shown that the commercial C-S-H phases used (Circosil®) are comparable to those produced by wet chemical methods. Only in the case of Cs(I) were slight deviations observed. However, such deviations are not uncommon in literature and can be attributed to conditions that vary depending on the study, such as the C/S ratio and structure of the solid phase, reversibility of the adsorption process, S/L ratio, salt content and the presence of competing ions. Under the conditions of the present study, moderate and irreversible retention of Cs(I) on Circosil® was determined, which also depends strongly on the prevailing ionic strength. Thus, in a 0.1 M NaCl solution, the retention was $75 \pm 1\%$, and in DGS ($I = 2.6$ M) only $14 \pm 1\%$. In contrast, however, no direct influence of the other WC elements on the Cs(I) retention behaviour was observed, so that additional studies in this regard would be advisable. Regarding Sm(III) and Eu(III), almost identical retention curves were observed, with the results also showed a strong affinity towards Circosil®. Thus, retention/adsorption on C-S-H phases is the preferred retention mechanism (compared to precipitation). In this regard, the kinetic of Sm(III) and Eu(III) retention indicated that surface complexation is probably the initial retention mechanism. Furthermore, the kinetics suggest competing effects of the other WC elements, which would need to be confirmed by additional experiments. Regarding U(VI), strong and irreversible retention on C-S-H phases was observed, which is only slightly influenced by the ionic strength and the other WC elements. In this context, the results suggest (partial) Ca(II)-mediated retention. Furthermore, possible precipitates, such as $\text{Na}_2\text{U}_2\text{O}_7$ or CaUO_4 , could be ruled out as an initial retention mechanism. However, additional investigations regarding the influence of the C/S ratio and the pH value on the immobilisation kinetics would be advisable [34].

Now that the retention mechanisms and some influencing factors of individual repository-relevant elements have been further clarified or at least better understood, the experimental setups should be reconsidered and, ideally, improved. The dynamic mini column approach here was to replace/supplement the standardised high-throughput batch method, which can only be understood as a rough model system due to static equilibria and unrealistic S/L, with a more realistic dynamic experimental setup. Therefore, in the next study, a new method for rapid and dynamic sorption experiments using HPLC, ICP-MS and HPLC-ICP-MS coupling was further developed – including a new approach for data evaluation. The refined and optimised MCE method was applied to investigate the retention of Cs(I) on Circosil® and that of Eu(III) on kaolinite and quartz sand. In the case of Cs(I) on

Circosil®, the results obtained were compared with those from batch experiments, which showed deviations in the $\log(R_d)$ values of max. 5.4% (between both methods). Furthermore, good agreement with literature data was obtained, so that the MCE approach can be considered validated. In addition, a data evaluation approach was also presented that enables the reliable calculation of common retention parameters (e.g. $q_{\max}$ or R_d) with excellent correlation coefficients. Next, the MCE method was further enhanced to enable an even faster online quantification using direct HPLC-ICP-QQQ coupling. This MCE-HPLC-ICP-QQQ was successfully applied to determine the $q_{\max}$ of Eu(III) on kaolinite and quartz sand. The values obtained were in excellent agreement with those in literature, so that this approach can also be considered verified. In summary, this study presents a new method (including data evaluation) for deriving dynamic retention coefficients and maximum loading capacities much faster, more resource-efficiently and more controllably than with conventional setups such as batch experiments. Furthermore, it is assumed that the MCE method can also be applied to a wider range of analytes and adsorption materials beyond repository research [12].

In the first two published studies, the understanding of retention mechanisms was further deepened and a new method for conducting retention and sorption studies was presented. Both aspects were now to be combined. Therefore, a comprehensive third (published) study was conducted, in which the remobilisation of the elements Si(IV), Ca(II), Mo(VI), Eu(III) and U(VI) incorporated in C-S-H phases was investigated. Until now, there has been little or no data on the remobilisation dynamics of such elements under conditions relevant to final HLW disposal and even less under realistic conditions (dynamic and suitable S/L ratio). The new MCE method offers a promising approach to close these gaps in knowledge. Therefore, Mo(VI), Eu(III) and U(VI) were added in two concentrations, both individually and as a mixture, during the synthesis of the C-S-H reaction solution. Subsequent XRD and ICP-QQQ confirmed successful synthesis and incorporation: Eu(III) and U(VI) quantitatively and Mo(VI) to approx. 50%. In initial investigations, these incorporated C-S-H phases were leached with ultrapure water in batch experiments and MCE. The results confirmed the expected leaching behaviour for Si(IV), Ca(II), Eu(III) and U(VI), with the latter two being remobilised only slightly or not at all. Mo(VI), on the other hand, was remobilised after only a few pore water exchange cycles, albeit not completely, suggesting two different retention mechanisms. All observations are consistent with data from batch experiments in the literature (where available), although stronger leaching/remobilisation behaviour of all elements was observed with the batch method. The reasons for this lie in the different equilibrium states of the pore water cycles and the different S/L ratios. It was therefore concluded that the MCE setup is more representative of the conditions in a potential repository, and thus all further experiments were conducted using MCEs only. This included investigating the influence of increased ionic strength (up to $I = 2 \text{ M}$), which showed no effect on Eu(III) and Mo(VI) leaching, but did result in a significant increase in Si(IV) and Ca(II) remobilisation, which, however, declined slightly at $I = 2 \text{ M}$ and could therefore be explained by the formation of Si(IV)-Ca(II) secondary phases. The also higher U(VI) remobilisation due to higher ionic strength was explained by the dissociation of Ca(II)-mediated sorption sites. In further MCEs the displacement agents Fe(III) and Tb(III) were injected into the eluents, to simulate further possible competition effects in a future repository. These had no influence on Eu(III) and U(VI) leaching but did influence the remobilisation behaviour of Si(IV), Ca(II) and Mo(VI). While Si(II) and Ca(II) leaching was significantly more pronounced, suggesting substitution in the C-S-H structure, the

remobilisation of Mo(VI) was significantly delayed, which in turn suggests the formation of poorly soluble trivalent metal molybdates. Last, the influence of the cement additive and complexing agent PBTC was investigated. The presence of PBTC increases the leaching of Si(IV), Ca(II), Eu(III) and U(VI), while that of Mo(VI) is slightly delayed. However, the mechanisms postulated in this context, such as the formation of a calcium phosphonate layer on the C-S-H surface, preferential complexation of Eu(III) and the formation of molybdenum calcium phosphonates, are still hypothetical and require further verification [8].

In all studies and investigations presented so far, retention mechanisms have been elucidated by determining the analyte concentrations in the supernatant solutions or the eluate. Due to the focus on method development, the method catalogue should also be expanded to include a method for quantifying trace elements in solid phases. The aim was to establish an LA-ICP-QQQ analysis method for detecting traces of repository-relevant elements in C-S-H phases, which can also be adapted to other construction and backfill materials in the future. During this, C-S-H standard materials in the form of pressed pellets with known analyte concentrations, mainly Mo(VI), Eu(III) and U(VI), were produced. After optimising the production procedure, these were used to develop a practical routine method for quantifying the trace elements in the solid phase. This allowed for a deviation in recovery of $\leq 10\%$ and can therefore be considered a reliable method. In addition to the common external calibration method, an elaborate calibration procedure was adapted and further developed, enabling a simple and resource-saving determination of elemental ratios in solids, like C-S-H phases. This so-called external SAM method was successfully applied to determine the C/S ratio of Circosil®, which was in excellent agreement with EDX and XRF results.

Although this work has closed many gaps in knowledge, presented new and more efficient analytical methods, and with that has made a significant contribution to (HLW) repository research, some questions remain unanswered and require further investigations. For example, regarding the kinetics study, it would be advisable to conduct additional comparative single-element and WC experiments, ideally also in less saline solutions and with higher concentrations of competing ions, to better understand the influence of the radioactive inventory itself. Furthermore, a Ca(II)-mediated U(VI) retention mechanism has been postulated several times, which could be clarified by additional spectroscopic investigations and, in the best case, supported by geochemical modelling. Regarding the remobilisation study, many retention, remobilisation, complexation and precipitation processes were assumed, which also require further clarification and thus investigations. In the case of excessive Si(IV) leaching, the formation of silicate agglomerates was assumed, to which Ca(II) can adsorb again. Also, the cleavage of a Ca(II)-mediated U(VI) retention mechanism at high ionic strengths is also postulated. The presumed calcium phosphonate layer, the assumed precipitation of poorly soluble trivalent metal molybdates and the preferred Eu(III) complexation are also purely hypothetical. All these hypotheses can be substantiated, refuted or confirmed by future experiments, ideally supported by spectroscopic analyses and geochemical modelling.

In the case of the newly developed MCE method, few questions remain unanswered so far. However, in future studies, the MCE method could be compared with those of frontal analysis, thereby clarifying, for example, the effects of possible concentration peaks caused by injection. Furthermore, it could be useful to adapt the MCE method to other analytes and adsorption materials, even outside of repository research, and thus establish dynamic sorption studies in many other fields.

Although the development of the LA-ICP-QQQ method via external calibration can be considered successful according to current standards, it would still be desirable to further improve the recovery rates (especially for U(VI)). To do so, additional studies would be useful to better understand potential fractionation effects. Apart from this, since both external SAM calibration methods have been successfully applied, adaptation to a broader spectrum of elements as well as construction and backfill materials (e.g. ettringite or kaolinite) would be useful.

Based on the experiments conducted in this work and the resulting findings, important new insights for the safety assessment for (HLW-) repositories could be gained. For example, decisive insights into the kinetics of the retention mechanisms of repository-relevant elements in construction and backfill materials were gained. Furthermore, based on the dynamic experimental approaches of this work, new mechanistic insights into the retention and remobilisation of radionuclides in and from C-S-H phases were shown, thus demonstrating the practicality of MCE as an efficient tool for final repository research. Most recently, a supplementary LA-ICP-QQQ analysis method was developed for quantifying trace elements in C-S-H phases, some of which can also be easily applied in other specialist areas.

5. References

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Use of artificial intelligence software

During the preparation of this work “NotebookLM” was used to facilitate literature research. NotebookLM is a closed (proprietary) AI tool that acts as an intelligent research assistant by analysing own uploaded documents and distilling complex content down to its essentials. The AI application was primarily used to make literature research clearer and more time efficient. All information suggested by the software from the literature sources fed into the system were checked again manually. Furthermore, the translation tool “DeepL” (latest used version 26.1.1.19426) was used to help with the translation and wording of some passages. After using this tool/service, the content was reviewed and edited as needed. The author takes full responsibility for the content of this work.

Appendix

Table_A 1: Manufacturer's information for the standard solutions used for all C-S-H synthesis.

Analyte	Manufacturer's specifications for the standard solution
Sc	1 g L ⁻¹ in 5% HNO ₃ , Alfa®, Karlsruhe, Germany
Y	1 g L ⁻¹ in 2–3% HNO ₃ , Merck Certipur®, Darmstadt, Germany
Zr	10 g L ⁻¹ in 7% HCl, Merck Supelco®, Darmstadt, Germany
Mo	1 g L ⁻¹ in 1 mol L ⁻¹ with traces HF, Bernd Kraft, Duisburg, Germany
Ru	1 g L ⁻¹ in 8% HCl, Merck, Darmstadt, Germany
Pd	1 g L ⁻¹ in ~ 1 M HNO ₃ , Fluka, Buchs, Switzerland
Cs	1 g L ⁻¹ in 2.5% HNO ₃ , AccuStandard, New Haven, USA
Sm	1 g L ⁻¹ in 5% HNO ₃ , Alfa Aesar Specpure®, Karlsruhe, Germany
Eu	10 g L ⁻¹ in diluted HNO ₃ , Agilent, Kingstown, USA
Ho	1 g L ⁻¹ in 2–3% HNO ₃ , Merck Certipur®, Darmstadt, Germany
U	1 g L ⁻¹ in 2–5% HNO ₃ , AccuStandard, New Haven, USA

Table_A 2: Calculated concentrations of Mo, Eu, and U and their deviations from the known value in the **WC-L_2** sample (45.9 µg g⁻¹ Mo, 149.9 µg g⁻¹ Eu and 219.2 µg g⁻¹ U) using the **syn C-S-H_2 RMs** (preparation see Table 6) at different laser powers (fluence = 3–10 J cm⁻²), the R² values of the individual calibration curves and the averaged RSD (averaged over the ablation lines, all RMs and all analytes at the respective fluence); 1150 W, [NoGas], 0.1 s integration time, 10 Hz, 10 µm s⁻¹, 50 x 50 µm spot size, 1.0 mm ablation lines.

Fluence	C _{Calc.} [µg g ⁻¹]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
3	36.3	115.4	180.4	-21.0	-23.0	-17.7	0.9896	0.9860	0.9839	2.36	3.91
4	34.6	115.8	183.1	-24.7	-22.7	-16.5	0.9887	0.9846	0.9847	2.11	1.58
5	36.6	116.0	187.9	-20.4	-22.6	-14.3	0.9912	0.9885	0.9889	1.77	1.17
6	38.6	114.3	194.4	-15.9	-23.7	-11.3	0.9912	0.9864	0.9869	4.00	5.55
7	40.0	120.0	206.8	-12.9	-19.9	-5.7	0.9940	0.9912	0.9914	2.17	1.96
8	45.5	153.1	220.0	-0.8	2.1	0.4	0.9936	0.9929	0.9932	2.77	2.86
9	45.8	135.9	226.3	-0.3	-9.4	3.2	0.9983	0.9933	0.9936	2.44	2.03
10	46.5	148.0	240.4	1.3	-1.3	9.7	0.9970	0.9900	0.9924	1.87	0.92

Appendix

Table_A 3: Repetition of the **WC-L_2** analysis using **syn C-S-H_2** RMs described in Table_A 2; all conditions are the same.

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
3	37.2	135.1	192.2	-19.0	-9.9	-12.3	0.9963	0.9911	0.9916	2.45	1.67
4	35.5	129.4	199.7	-22.5	-13.7	-8.9	0.9685	0.9905	0.9908	6.16	14.28
5	40.3	183.6	205.6	-12.2	22.5	-6.2	0.9982	0.9931	0.9944	1.81	1.65
6	44.3	146.8	233.8	-3.5	-2.1	6.7	0.9968	0.9936	0.9932	1.96	1.45
7	51.2	145.9	245.5	11.6	-2.6	12.0	0.9985	0.9960	0.9963	2.07	1.85
8	49.8	180.6	262.0	8.5	20.5	19.5	0.9994	0.9997	1.0000	3.98	6.47
9	52.9	191.1	271.0	15.4	27.5	23.6	0.9988	0.9975	0.9977	4.90	9.00
10	51.1	176.2	276.5	11.3	17.6	26.1	0.9995	0.9990	0.9989	3.19	4.00

Table_A 4: Repetition of the **WC-L_2** analysis using **syn C-S-H_2** RMs described in Table_A 2 (and Table_A 3) but with measurement in [He] collision gas mode; the rest of the conditions are the same as described in Table_A 2.

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
3	37.8	127.4	204.5	-17.7	-15.0	-6.7	0.9959	0.9949	0.9944	3.41	5.72
4	38.7	138.6	211.2	-15.6	-7.5	-3.6	0.9949	0.9931	0.9910	1.82	1.25
5	42.6	143.3	224.0	-7.1	-4.4	2.2	0.9960	0.9878	0.9874	3.29	6.86
6	45.8	147.7	249.8	-0.2	-1.5	14.0	0.9970	0.9911	0.9911	4.27	10.32
7	51.4	172.1	277.2	12.1	14.8	26.4	0.9997	0.9939	0.9943	2.38	2.76
8	57.3	178.4	297.7	25.0	19.0	35.8	0.9996	0.9975	0.9979	2.63	2.64
9	57.3	172.6	298.3	24.9	15.2	36.1	0.9998	0.9993	0.9993	2.55	2.22
10	56.1	182.9	287.6	22.4	22.0	31.2	0.9993	0.9983	0.9977	3.79	5.65

Table_A 5: Repetition of the **WC-L_2** analysis using **syn C-S-H_2** RMs described in Table_A 4; all conditions are the same.

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
3	34.7	120.6	185.5	-24.4	-19.6	-15.4	0.9956	0.9917	0.9906	2.87	2.71
4	35.3	110.1	193.4	-23.0	-26.6	-11.8	0.9957	0.9949	0.9950	2.34	2.18
5	38.0	119.3	203.2	-17.1	-20.4	-7.3	0.9969	0.9932	0.9931	1.62	0.98
6	41.8	137.3	223.1	-8.9	-8.4	1.8	0.9932	0.9938	0.9948	4.31	4.36
7	47.2	157.6	253.3	2.8	5.1	15.6	0.9976	0.9973	0.9977	4.39	6.42
8	51.4	160.4	263.5	12.0	7.0	20.2	1.0000	0.9981	0.9990	3.66	2.82
9	51.8	147.4	246.5	12.9	-1.7	12.4	0.9995	0.9956	0.9968	2.13	0.92
10	51.9	153.1	262.3	13.1	2.1	19.7	0.9989	0.9955	0.9964	2.26	1.35

Appendix

*Table_A 6: Calculated concentrations of Mo, Eu, and U and their deviations from the known value in the **WC-L_2** sample ($45.9 \mu\text{g g}^{-1}$ Mo, $149.9 \mu\text{g g}^{-1}$ Eu and $219.2 \mu\text{g g}^{-1}$ U) using the **syn C-S-H_1 RMs** (preparation see Table 6) at different laser powers (fluence = $3\text{--}10 \text{ J cm}^{-2}$), the R^2 values of the individual calibration curves and the averaged RSD (averaged over the ablation lines, all RMs and all analytes at the respective fluence); 1150 W, [He] (collision gas mode), 0.1 s integration time, 10 Hz, $10 \mu\text{m s}^{-1}$, $50 \times 50 \mu\text{m}$ spot size, 1.0 mm ablation lines.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
3	30.6	120.2	174.1	-33.3	-19.8	-20.6	0.9924	0.9991	0.9986	2.79	1.80
4	35.2	121.7	191.3	-23.2	-18.8	-12.7	0.9981	0.9973	0.9976	2.52	1.22
5	39.6	129.1	211.1	-13.7	-13.8	-3.7	0.9976	0.9932	0.9979	4.90	11.36
6	44.9	152.1	247.9	-2.1	1.5	13.1	0.9957	0.9992	0.9988	2.58	0.98
7	52.4	148.3	260.6	14.2	-1.0	18.9	0.9921	0.9993	0.9992	2.75	2.26
8	58.9	206.2	301.0	28.4	37.6	37.3	0.9992	0.9999	0.9997	2.09	0.72
9	59.8	195.3	320.4	30.4	30.3	46.2	0.9973	0.9987	0.9995	2.71	1.65
10	61.0	203.3	323.5	33.1	35.6	47.6	0.9990	0.9993	0.9998	2.33	1.37

*Table_A 7: Repetition of the **WC-L_2** analysis using **syn C-S-H_1 RMs** described in Table_A 6; all conditions are the same.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
3	29.4	89.0	150.0	-35.8	-40.6	-31.6	0.9983	0.9943	0.9982	2.37	1.20
4	33.9	95.2	170.2	-26.1	-36.5	-22.3	0.9983	0.9984	0.9994	2.23	1.16
5	38.0	103.6	191.3	-17.1	-30.9	-12.7	0.9988	0.9997	0.9999	2.18	1.09
6	46.8	124.0	223.8	2.0	-17.2	2.1	0.9982	0.9996	0.9994	2.35	1.20
7	50.9	170.6	257.5	11.0	13.8	17.5	0.9986	0.9998	0.9998	2.31	1.26
8	55.4	154.7	272.0	20.8	3.2	24.1	0.9992	0.9998	0.9999	2.34	1.23
9	57.3	163.4	288.3	24.9	9.0	31.5	0.9993	0.9984	0.9988	2.57	2.11
10	60.5	189.4	310.2	32.0	26.4	41.5	0.9990	0.9994	0.9995	2.23	0.80

*Table_A 8: Same **WC-L_2** analysis using **syn C-S-H_2 RMs** described in Table 16 but without a normalisation to the ^{43}Ca signals; the rest of the conditions are the same as described in Table 16.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
5	41.5	113.9	208.6	-9.6	-24.0	-4.8	0.9995	0.9998	0.9999	3.10	2.69
6	43.3	134.8	218.5	-5.7	-10.1	-0.3	0.9972	0.9990	0.9988	5.38	9.58
7	40.4	124.2	214.4	-12.0	-17.1	-2.2	0.9991	0.9983	0.9988	3.52	3.46
8	39.5	120.7	202.9	-13.9	-19.5	-7.5	0.9997	0.9998	0.9998	3.14	2.35

Appendix

*Table_A 9: Calculated concentrations of Mo, Eu, and U and their deviations from the known value in the **WC-L_2** sample ($45.86 \mu\text{g g}^{-1}$ Mo, $149.87 \mu\text{g g}^{-1}$ Eu and $219.2 \mu\text{g g}^{-1}$ U) using the **syn C-S-H_3 RMs** (preparation Table 6) at different laser powers (fluence = $4\text{--}9 \text{ J cm}^{-2}$), the R^2 values of the individual calibration curves and the averaged RSD (averaged over the ablation lines, all RMs and all analytes at the respective fluence); 1150 W, [He] (collision gas mode), 0.1 s integration time, 10 Hz, $10 \mu\text{m s}^{-1}$, $50 \times 50 \mu\text{m}$ spot size, 1.0 mm ablation lines.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
4	44.1	142.2	188.7	-3.8	-5.1	-13.9	0.9987	0.9867	0.9992	3.11	3.62
5	43.3	179.3	199.0	-5.5	19.7	-9.2	0.9703	0.9552	0.9998	8.95	11.83
6	49.6	153.7	204.8	8.1	2.5	-6.6	0.9981	0.9972	0.9989	5.13	6.64
7	55.5	178.2	230.6	21.0	18.9	5.2	0.9998	0.9977	0.9999	5.30	6.43
8	55.0	216.6	237.0	19.9	44.5	8.1	0.9997	0.9047	0.9978	3.49	2.56
9	63.5	183.3	241.9	38.5	22.3	10.3	0.9997	0.9841	0.9991	3.73	4.41

*Table_A 10: Calculated concentrations of Mo, Eu, and U and their deviations from the known value in the **syn C-S-H_3 Control** sample ($10.0 \mu\text{g g}^{-1}$ Mo, $10.0 \mu\text{g g}^{-1}$ Eu and $10.0 \mu\text{g g}^{-1}$ U) using the **syn C-S-H_3 RMs** (preparation see Table 6) at different laser powers (fluence = $4\text{--}9 \text{ J cm}^{-2}$), the R^2 values of the individual calibration curves and the averaged RSD (averaged over the ablation lines, all RMs and all analytes at the respective fluence); 1150 W, [He] (collision gas mode), 0.1 s integration time, 10 Hz, $10 \mu\text{m s}^{-1}$, $50 \times 50 \mu\text{m}$ spot size, 1.0 mm ablation lines.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]		
	Mo	Eu	U	Mo	Eu	U
4	10.0	9.6	9.4	-0.1	-4.5	-5.8
5	11.0	10.3	10.0	10.3	2.5	-0.1
6	10.8	10.8	10.4	8.3	7.6	4.4
7	11.2	10.9	10.6	12.4	8.5	6.0
8	12.0	11.9	11.4	20.4	18.6	14.0
9	12.0	12.5	12.1	20.3	24.8	20.5

*Table_A 11: Same **WC-L_2** analysis using **syn C-S-H_3 RMs** described in Table_A 9 but using a normalisation to the summed signal of ^{30}Si and ^{43}Ca ; the rest of the conditions are the same as described in Table_A 9.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
4	47.8	154.2	204.4	4.1	2.9	-6.7	0.9992	0.9841	0.9996	3.11	3.62
5	45.1	185.9	205.9	-1.7	24.0	-6.1	0.9723	0.9577	0.9998	8.95	11.83
6	52.8	165.8	221.8	15.1	10.6	1.2	0.9997	0.9855	0.9991	5.13	6.64
7	51.2	164.3	212.4	11.6	9.6	-3.1	1.0000	0.9982	1.0000	5.30	6.43
8	48.5	189.7	206.6	5.6	26.6	-5.7	0.9990	0.9379	1.0000	3.49	2.56
9	52.8	151.5	199.5	15.2	1.1	-9.0	0.9995	0.9931	0.9999	3.73	4.41

Appendix

*Table_A 12: Same **syn C-S-H_3 Control** analysis using **syn C-S-H_3 RMs** described in Table_A 10 but using a normalisation to the summed signal of ^{30}Si and ^{43}Ca ; the rest of the conditions are the same as described in Table_A 10.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]		
	Mo	Eu	U	Mo	Eu	U
4	11.1	10.9	10.6	10.7	8.8	5.5
5	11.7	11.0	10.7	16.8	10.0	6.6
6	11.0	11.0	10.7	10.2	9.8	6.8
7	11.3	10.9	10.7	13.2	9.3	7.3
8	11.3	11.0	10.7	13.1	9.6	7.3
9	11.0	11.1	11.0	9.6	11.1	9.9

*Table_A 13: Same **WC-L_2** analysis using **syn C-S-H_3 RMs** described in Table_A 9 but using a normalisation to the summed signal of ^{30}Si and ^{44}Ca ; the rest of the conditions are the same as described in Table_A 9.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]			R ²			Avg. RSD [%]	
	Mo	Eu	U	Mo	Eu	U	Mo	Eu	U	$\bar{X}$	σ
4	44.2	143.1	190.4	-3.6	-4.5	-13.1	0.9998	0.9792	1.0000	3.11	3.62
5	41.2	171.5	190.6	-10.2	14.5	-13.0	0.9671	0.9507	0.9999	8.95	11.83
6	46.8	146.5	196.0	2.0	-2.2	-10.6	1.0000	0.9903	0.9999	5.13	6.64
7	46.9	151.3	195.8	2.3	0.9	-10.7	0.9998	0.9973	1.0000	5.30	6.43
8	44.8	175.8	192.1	-2.2	17.3	-12.4	0.9995	0.9314	1.0000	3.49	2.56
9	50.0	143.7	189.6	8.9	-4.1	-13.5	0.9998	0.9909	1.0000	3.73	4.41

*Table_A 14: Same **syn C-S-H_3 Control** analysis using **syn C-S-H_3 RMs** described in Table_A 10 but using a normalisation to the summed signal of ^{30}Si and ^{44}Ca ; the rest of the conditions are the same as described in Table_A 10.*

Fluence	C _{Calc.} [$\mu\text{g g}^{-1}$]			Deviation [%]		
	Mo	Eu	U	Mo	Eu	U
4	10.4	10.1	9.9	4.2	0.7	-1.3
5	10.9	10.1	9.9	9.4	1.0	-1.0
6	10.2	10.0	9.9	2.2	-0.1	-1.5
7	10.4	9.8	9.8	3.7	-2.3	-2.4
8	10.4	9.8	9.8	3.6	-2.1	-2.5
9	10.0	9.9	9.9	-0.4	-1.5	-0.7

Table_A 15: Manufacturer's information for the standard solutions and HNO₃ used for dual sample/standard analysis of NIST® SRM® 612 after O'Connor et al. [168] and the adapted external SAM analysis of Circosil®.

Analyte	Manufacturer's specifications for the standard solution
HNO ₃	Supra 69 %, Carl Roth Rotipuran®, Karlsruhe, Germany
Si	10 g L ⁻¹ in water. Tr. HF, AccuStandard, New Haven, USA
Ca	1 g L ⁻¹ in 0.5 mol L ⁻¹ HNO ₃ , Merck Certipur®, Darmstadt, Germany
Sc	1 g L ⁻¹ in 5% HNO ₃ , Alfa®, Karlsruhe, Germany
Ti	1 g L ⁻¹ in water. Tr. HF, VWR® Prolabo®, Lutterworth Leicestershire, England
Fe	1 g L ⁻¹ in 2–3 % HNO ₃ , Merck Certipur®, Darmstadt, Germany
Co	1 g L ⁻¹ in 0.5 mol L ⁻¹ HNO ₃ , Merck Certipur®, Darmstadt, Germany
Cu	1 g L ⁻¹ in ~ 0.05 M HNO ₃ , Fluka, Buchs, Switzerland
Ho	1 g L ⁻¹ in 2–3% HNO ₃ , Merck Certipur®, Darmstadt, Germany
Tl	1 g L ⁻¹ in 2% HNO ₃ , Carl Roth ROTI®STAR, Karlsruhe, Germany
U	1 g L ⁻¹ in 2–5% HNO ₃ , AccuStandard, New Haven, USA

Table_A 16: Parameters/variables obtained from the underground corrected but not normalised external SAM analysis of the NIST® 612 standard material, where $C_{A/NIST}^S$ = known concentration of the analyte in the NIST® SRM®; measurement conditions see Figure 36.

Element	$C_{A/0}^L$ [µg L ⁻¹]	S_A^L [CPS L µg ⁻¹]	S_A^{S+L} [CPS L µg ⁻¹]	$\frac{\dot{m}_A^L}{\dot{m}_A^S}$	$C_{A/NIST}^S$ [µg kg ⁻¹]
Ti	-24.505	1,475	1367	1895.19	50,100
Co	-18.994	27,401	25,640	1748.92	35,500
Cu	-22.627	14,586	13,665	1560.93	37,700
Tl	-7.797	46,794	44,928	1933.28	15,700
U	-18.787	59,0756	59,134	1991.67	37,380

Table_A 17: Parameters/variables obtained from the not underground corrected but normalised external SAM analysis of the NIST® 612 standard material, where $C_{A/NIST}^S$ = known concentration of the analyte in the NIST® SRM®; measurement conditions see Figure 36.

Element	$C_{A/0}^L$ [µg L ⁻¹]	S_A^L [CPS L µg ⁻¹]	S_A^{S+L} [CPS L µg ⁻¹]	$\frac{\dot{m}_A^L}{\dot{m}_A^S}$	$C_{A/NIST}^S$ [µg kg ⁻¹]
Ti	-22.89	0.00510	0.00204	875.96	50,100
Co	-17.68	0.09475	0.03816	808.65	35,500
Cu	-21.26	0.05043	0.02038	716.53	37,700
Tl	-7.62	0.06648	0.02665	826.01	15,700
U	-18.52	0.08392	0.03508	843.54	37,380

Appendix

Table_A 18: Parameters/variables obtained from the not underground corrected and not normalised external SAM analysis of the NIST® 612 standard material, where $C_{A/NIST}^S$ = known concentration of the analyte in the NIST®SRM®; measurement conditions see Figure 36.

Element	$C_{A/0}^L$ [$\mu\text{g L}^{-1}$]	S_A^L [CPS L μg^{-1}]	S_A^{S+L} [CPS L μg^{-1}]	$\frac{\dot{m}_A^L}{\dot{m}_A^S}$	$C_{A/NIST}^S$ [$\mu\text{g kg}^{-1}$]
Ti	-24.597	1,475	1,367	1,888.2	50,100
Co	-19.009	27,401	25,640	1,747.5	35,500
Cu	-22.832	14,586	13,665	1,547.0	37,700
Tl	-7.800	46,794	44,928	1,932.6	15,700
U	-18.788	59,076	59,134	1,991.5	37,380

Table_A 19: Calculated concentrations in the NIST® 612 ($C_{A/calc}^S$) using Equation 12 and the values listed in Table_A 16 (with underground correction but without normalisation); for each mass flow ratio listed there, the resulting concentrations and the absolute deviation (Δ) were calculated for all analytes (the certified values ($C_{A/NIST}^S$) are also shown in Table_A 16).

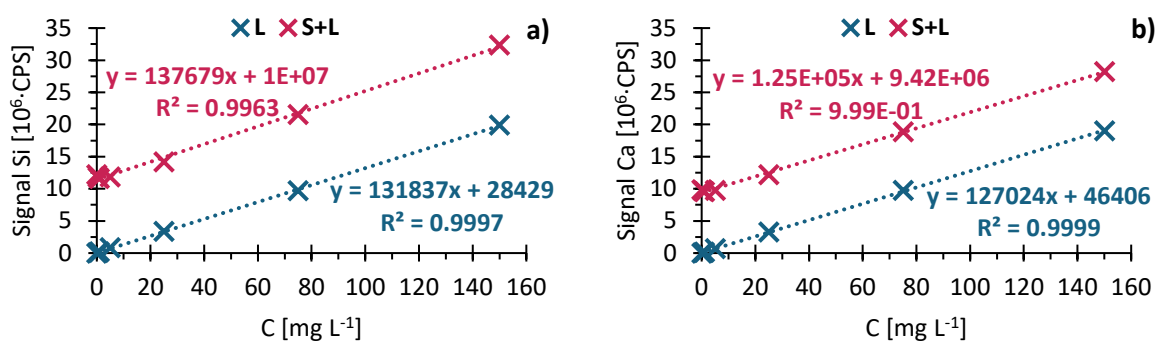
Element	Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Ti		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Co		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Cu		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Tl		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of U	
	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]
Ti	50,100	0.00	46,112	7.96	41,198	17.77	47,080	6.03	47,080	6.03
Co	38,571	8.65	35,500	0.00	31,717	10.66	36,246	2.10	36,246	2.10
Cu	45,846	21.61	42,196	11.93	37,700	0.00	43,083	14.28	43,083	14.28
Tl	16,707	6.41	15,377	2.06	13,738	12.49	15,700	0.00	15,700	0.00
U	38,961	4.23	35,860	4.07	32,039	14.29	36,613	2.05	36,613	2.05

Table_A 20: Calculated concentrations in the NIST® 612 ($C_{A/calc}^S$) using Equation 12 and the values listed in Table_A 17 (without underground correction but with normalisation); for each mass flow ratio listed there, the resulting concentrations and the absolute deviation (Δ) were calculated for all analytes (the certified values ($C_{A/NIST}^S$) are also shown in Table_A 17).

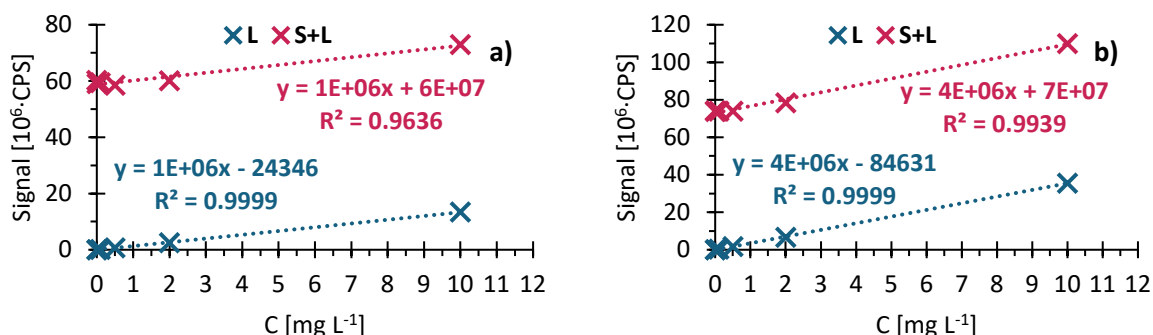
Element	Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Ti		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Co		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Cu		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of Tl		Calc. from $\frac{\dot{m}_A^L}{\dot{m}_A^S}$ of U	
	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]
Ti	50,100	0.00	46,250	7.68	40,981	18.20	47,243	5.70	48,246	3.70
Co	38,455	8.32	35,500	0.00	31,456	11.39	36,262	2.15	37,032	4.31
Cu	46,089	22.25	42,547	12.86	37,700	0.00	43,461	15.28	44,383	17.73
Tl	16,649	6.05	15,370	2.10	13,619	13.25	15,700	0.00	16,033	2.12
U	38,817	3.84	35,834	4.14	31,752	15.06	36,603	2.08	37,380	0.00

Table_A 21: Calculated concentrations in the NIST® 612 ($C_{A/calc}^S$) using Equation 12 and the values listed in Table_A 18 (without underground correction and normalisation); for each mass flow ratio listed there, the resulting concentrations and the absolute deviation (Δ) were calculated for all analytes (the certified values ($C_{A/NIST}^S$) are also shown in Table_A 18).

Element	Calc. from $\frac{\dot{m}_A}{\dot{m}_S}$ of Ti		Calc. from $\frac{\dot{m}_A}{\dot{m}_S}$ of Co		Calc. from $\frac{\dot{m}_A}{\dot{m}_S}$ of Cu		Calc. from $\frac{\dot{m}_A}{\dot{m}_S}$ of Tl		Calc. from $\frac{\dot{m}_A}{\dot{m}_S}$ of U	
	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]	$C_{A/calc}^S$ [$\mu\text{g kg}^{-1}$]	Δ [%]
Ti	50,100	0.00	46,367	7.45	41,045	18.07	51,278	2.35	52,842	5.47
Co	38,358	8.05	35,500	0.00	31,425	11.48	39,260	10.59	40,457	13.96
Cu	46,017	22.06	42,588	12.97	37,700	0.00	47,099	24.93	48,535	28.74
Tl	15,339	2.30	14,196	9.58	12,567	19.96	15,700	0.00	16,179	3.05
U	35,441	5.19	32,800	12.25	29,035	22.32	36,274	2.96	37,380	0.00



Figure_A 1: Calibration curves of a) ^{28}Si and b) ^{44}Ca from external SAM of Circosil®; with L = calibration curve from solution (concentration 0, 0.5, 1, 5, 25, 75, and 150 mg L⁻¹) and S+L = calibration curve from solution while ablating; nebuliser gas flow 1.1 L min⁻¹, 1550 W, [H₂]-mode (5.8 mL min⁻¹), 0.1 s integration time, 2 J cm⁻², 10 Hz, 10 $\mu\text{m s}^{-1}$, 50 μm $\varnothing$ spot size, data acquisition time 165 s.



Figure_A 2: Calibration curves of a) ^{56}Fe and b) ^{59}Co from external SAM of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$; with L = calibration curve from solution (concentration 0, 0.005, 0.1, 0.5, 2 and 10 150 mg L⁻¹) and S+L = calibration curve from solution while ablating; nebuliser gas flow 1.1 L min⁻¹, 1550 W, [He]-mode (6.0 mL min⁻¹), 0.1 s integration time, 1.04 J cm⁻², 10 Hz, 10 $\mu\text{m s}^{-1}$, 30 μm $\varnothing$ spot size, 600 μm ablation lines.

Table_A 22: Parameters/variables obtained from the underground corrected and not normalised external SAM analysis of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$; measurement conditions see Figure_A 2.

Element	$C_{A/o}^L$ [$\mu\text{g L}^{-1}$]	S_A^L [CPS L μg^{-1}]	S_A^{S+L} [CPS L μg^{-1}]
Fe	-42.589	1,336,397	1,380,293
Co	-19.912	3,554,620	3,663,416