Chemical reactivity of $\alpha$-isosaccharinic acid in heterogeneous alkaline systems

November 2008

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Paul Scherrer Institut, Villigen PSI
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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.
PREFACE

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the partial financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>ACW-I</td>
<td>Artificial cement pore water (representing the ‘first stage’ of cement degradation)</td>
</tr>
<tr>
<td>α-ISA</td>
<td>α-isosaccharinic acid. Isosaccharinic acid is a general term for 3-deoxy-2-C-(hydroxymethyl)-aldonic acids. In the present report the term isosaccharinic acid is used for simplicity for the glucoisosaccharinic acids. Note that these names are in plural because several stereoisomeric forms may exist.</td>
</tr>
<tr>
<td>HCP</td>
<td>Hardened cement paste</td>
</tr>
<tr>
<td>HPAEC</td>
<td>High performance anion exchange chromatography&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>HPCEC</td>
<td>High performance cation exchange chromatography</td>
</tr>
<tr>
<td>HPIEC</td>
<td>High performance ion exclusion chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma-optical emission spectroscopy</td>
</tr>
<tr>
<td>NPOC</td>
<td>Non-purgeable organic carbon</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>S/L</td>
<td>Solid to liquid ratio</td>
</tr>
</tbody>
</table>

<sup>1</sup> The addition ‘cond’ denotes conductometric detection, the addition ‘PAD’ pulsed amperometric detection
ABSTRACT

Cellulose degradation under alkaline conditions is of relevance for the mobility of many radionuclides in the near-field of a cementitious repository for radioactive waste, because metal-binding degradation products may be formed. Among these α-isosaccharinic acid (α-ISA) is the strongest complexant. The prediction of the equilibrium concentration of α-ISA in cement pore water is therefore an important step in the assessment of the influence of cellulose degradation products on the speciation of radionuclides in such environments.

The present report focuses on possible chemical transformation reactions of α-ISA in heterogeneous alkaline model systems containing either Ca(OH)$_2$ or crushed hardened cement paste. The transformation reactions were monitored by measuring the concentration of α-ISA by high performance anion exchange chromatography and the formation of reaction products by high performance ion exclusion chromatography. The overall loss of organic species from solution was monitored by measuring the concentration of non-purgeable organic carbon. The reactions were examined in diluted and compacted suspensions, either at 25 °C or 90 °C, and under anaerobic atmospheres obtained by various methods. It was found that α-ISA was transformed under all conditions tested to some extent. Reaction products, such as glycolate, formate, lactate and acetate, all compounds with less complexing strength than α-ISA, were detected. The amount of reaction products identified by the chromatographic technique applied was ~50 % of the amount of α-ISA reacted. Sorption of α-ISA to Ca(OH)$_2$ contributed only to a minor extent to the loss of α-ISA from the solution phase.

As the most important conclusion of the present work it was demonstrated that the presence of oxidising agents had a distinctive influence on the turnover of α-ISA. Under aerobic conditions α-ISA was quantitatively converted to reaction products, whereas under strict anaerobic conditions, only small amounts of α-ISA were transformed. It can be hypothesised that, under these conditions, either traces of oxygen remaining bound to Ca(OH)$_2$ or unidentified impurities in Ca(OH)$_2$ were responsible for the reactions observed. The involvement of microbially mediated processes can be excluded, because the reactions proceeded in a similar qualitative manner, however faster, at 90 °C than at room temperature.

The possible chemical degradation of α-ISA to organic compounds with less complexation capabilities under anaerobic repository conditions is therefore not supported by the experimental findings of the present study.
ZUSAMMENFASSUNG

Der Abbau von Cellulose unter alkalischen Bedingungen ist für die Mobilität zahlreicher Radionuklide im Nahfeld eines zementhaltigen geologischen Tiefenlagers für radioaktive Abfälle von Bedeutung, weil die Abbauprodukte metallbindende Eigenschaften aufweisen können. Der stärkste Ligand, welcher hierbei gebildet wird, ist die α-Isosaccharinsäure (α-ISA). Die Quantifizierung der Gleichgewichtskonzentration von α-ISA im Zementporenwasser ist deshalb ein wichtiger Schritt bei der Beurteilung des Einflusses der Cellulose auf die Nuklidspeziation in einer solchen chemischen Umgebung.


Als wichtigste Schlussfolgerung dieser Arbeit konnte gezeigt werden, dass die Anwesenheit von Oxidationsmitteln einen markanten Einfluss auf den Reaktionsumsatz hatte. Unter Luftatmosphäre wurde die Gesamtmengen vorgelegter α-ISA in Reaktionsprodukte umgewandelt, unter stark anaeroben Bedingungen hingegen nur kleinere Anteile. Aufgrund der gemessenen Daten kann man mutmassen, dass Spuren von Sauerstoff, welche dem Ca(OH)$_2$ anhafteten, oder nicht-identifizierte oxidierende Verunreinigungen im Ca(OH)$_2$ für die beobachteten Reaktionen unter anaeroben Bedingungen verantwortlich waren. Der Einfluss von mikrobiellen Prozessen kann ausge schlossen werden, weil die beobachteten Reaktionen bei 90 °C in qualitativer Hinsicht ähnlich abliefen wie bei Raumtemperatur, nur mit einer höheren Reaktionsrate.

Im Hinblick auf eine Anwendung der Resultate im Rahmen einer Sicherheitsanalyse für ein geologisches Tiefenlager, welches größere Anteile an Zement enthält, lassen es die gemessenen Daten als unwahrscheinlich erscheinen, dass die Gleichgewichtskonzentration von α-ISA im Zementporenwasser unter relevanten anaeroben in-situ Bedingungen durch chemische Transformationsreaktionen markant herabgesetzt wird.
RESUME

Dans le cadre d’un stockage en béton de déchets radioactifs, la dégradation de la cellulose en conditions alcalines pourrait fortement influencer la mobilité de plusieurs radionucléides par la formation de complexes métalliques. En effet, dans ces conditions, le ligand de plus fort pouvoir complexant qui peut être produit, est l’acide isosaccharinique (α-ISA). C’est pourquoi, la connaissance de sa concentration à l’équilibre dans une eau interstitielle de ciment est une démarche essentielle afin de mieux apprécier les effets de la dégradation de la cellulose sur la spéciation des radionucléides.

Dans le cadre de ce rapport, les réactions chimiques possibles de transformation de l’α-ISA ont été étudiées dans des systèmes alcalins modèles, contenant soit de Ca(OH)$_2$ soit de la pâte durcie de ciment. Ces réactions ont été suivies à l’aide de mesures de la concentration de l’α-ISA en utilisant la chromatographie par échange d’anions à haute performance. Par ailleurs, les produits issus de ces mêmes réactions ont été caractérisés à l’aide de la chromatographie par exclusion des ions à haute performance. Les mesures des concentrations en carbone organique en solution ont permis de mettre en évidence la diminution de la concentration des espèces organiques. Les expériences ont été conduites dans des suspensions diluées ou concentrées, à température ambiante ou à 90°C et dans différentes conditions d’anaérobie.

Dans tous les cas, nous avons constaté que l’α-ISA réagissait mais pas totalement, en formant du glycolate, formate, lactate et acétate. Ces produits sont des substances avec un faible pouvoir complexant. La proportion des produits identifiés correspond à ~50 % de la quantité de l’α-ISA qui a réagi. La sorption de l’α-ISA par Ca(OH)$_2$ ne peut expliquer qu’en faible partie la diminution de la concentration de l’α-ISA de la solution.

Cette étude nous a particulièrement permis de démontrer que la présence des oxydants avait une forte influence sur le rendement de la réaction de transformation de l’α-ISA en conditions alcalines. En condition atmosphérique normale, la réaction de transformation de l’α-ISA est totale. Sous atmosphère anaérobique, cette réaction n’est que partielle. On peut donc supposer que des traces d’oxygène adsorbées à la surface de Ca(OH)$_2$ ou des impuretés non identifiées présentes initialement dans le Ca(OH)$_2$ ont été responsables des réactions observées en conditions anaérobiques. Par contre, l’influence des microbes sur ces processus peut être exclu dans notre cas. En effet, les transformations observées à 90 °C étaient comparables qualitativement à celles effectuées à 25 °C, sauf en terme de cinétique : la réaction à haute température a été plus rapide que celle à 25°C.

Dans l’objectif de l’application de ces résultats dans une étude globale d’évaluation de performances d’un site de stockage de déchets radioactifs en milieu cimentaire, on peut conclure que les transformations chimiques de l’α-ISA n’ont probablement pas un effet significatif sur la diminution de sa concentration à l’équilibre dans l’eau interstitielle de ciment.
1  INTRODUCTION

1.1  Scope and aims of the work

Cellulose is an important organic component in low- and intermediate level radioactive wastes. The chemical degradation of cellulosic material in a cementitious environment results in the formation of water-soluble species. \(\alpha\)-isosaccharinic acid (\(\alpha\)-ISA), one of the most important degradation products (WHISTLER & BEMILLER, 1958; VAN LOON & GLAUS, 1998; GLAUS et al., 1999; KNILL & KENNEDY, 2003; PAVASARS et al., 2003), is a strong complexant at alkaline conditions towards many cations of the transition metal, lanthanide and actinide series (BASTON et al., 1994; GREENFIELD et al., 1995; BOURBON & TOULHOAT, 1996; VAN LOON et al., 1999; VERCAMMEN et al., 2001; ALLARD & EKBERG, 2006; WARWICK et al., 2006). Complexation of radionuclides by water-soluble compounds leads to a decrease in their sorption and an increase in their solubility. Cellulose degradation products may thus have a detrimental effect on the chemical barrier function of concrete with respect to migration of heavy metal ions or radionuclides (ASKARIEH et al., 2000; VAN LOON & GLAUS, 1998). The alkaline degradation of cellulose leads to almost equal concentrations of \(\alpha\)-ISA and \(\beta\)-isosaccharinic acid, a diastereomeric form of \(\alpha\)-ISA. The complexation strength of \(\beta\)-isosaccharinic acid is, however, \(\sim\)2 orders of magnitude lower than the one of \(\alpha\)-ISA (VAN LOON & GLAUS, 1998). Therefore the scope of the present report is focused on experiments with \(\alpha\)-ISA.

For the safety assessment of a cementitious repository for radioactive waste containing substantial amounts of cellulose, it is important to know the solution concentration of \(\alpha\)-ISA as a function of various parameters, such as the amount of cellulose, amount of cement, reactivity of \(\alpha\)-ISA towards solid phases in cement, etc. One aspect that has been treated only marginally in the past is the chemical long-term stability of \(\alpha\)-ISA under the conditions of cement pore water and in the presence of the various mineral phases contained in cement. Indications in the literature for a chemical transformation of \(\alpha\)-ISA go back to 1930, when BERNHAUER & WOLF (1930) investigated the formation of lactic acid from a series of sugars and related compounds in the presence of CaO at temperatures up to 190 °C and reduced pressure. They observed a significant formation of lactic acid also from \(\alpha\)-ISA. ALFREDSSON et al. (1961) noted that the disappearance of \(\alpha\)-ISA under oxic conditions at 170 °C in \(\sim\)1.7 M NaOH occurred within \(\sim\)20 days. However, no reaction products were characterised in that work. Indications for partial transformation of \(\alpha\)-ISA to unidentified compounds was also
described by FEAST et al. (1965), who treated \( \alpha \)-ISA under alkaline conditions at 97 °C for 4 hours. GREENFIELD et al. (1995) and HURDUS & PILKINGTON (2000), who carried out their experiments in homogeneous alkaline solutions at room temperature and 80 °C, observed a slight transformation of \( \alpha \)-ISA under oxic conditions, whereas no transformation was detected under anoxic conditions. In our previous studies (VAN LOON & GLAUS, 1998), the chemical stability of \( \alpha \)-ISA has only been assessed under exclusion of oxygen in a homogenous artificial cement pore water. No transformation of \( \alpha \)-ISA could be detected in such systems. However, in recent cellulose degradation experiments carried out in the presence of Ca(OH)\(_2\) at temperatures of 60 °C and 90 °C (GLAUS & VAN LOON, 2004a), a transformation of \( \alpha \)-ISA to low molecular weight carboxylic acids has been noticed.

Little is thus known about the chemical fate of \( \alpha \)-ISA in heterogeneous alkaline suspensions, which may better simulate the real situation of \( \alpha \)-ISA in cementitious systems. A project was therefore co-funded between Nagra, Nirex (now incorporated into the NDA), SKB and PSI with the main goals (i) to identify the circumstances, under which chemical transformation of \( \alpha \)-ISA may take place, (ii) to identify possible degradation products and characterise their influence on radionuclide speciation, and (iii) to examine to what extent the results from these laboratory experiments may be transferred to repository conditions. Accordingly, a series of long-term experiments were carried out at PSI. The present report gives a detailed overview of these experiments and the results obtained.

In all tests, solutions of \( \alpha \)-ISA in synthetic cement pore water were exposed to a solid, being either Ca(OH)\(_2\) or crushed hardened cement paste (HCP). Ca(OH)\(_2\) is a main mineral phase of cement and was mainly tested because it was present in the above mentioned cellulose degradation experiments. HCP was tested in view of a possible application of the results for the safety case of a repository for low- and intermediate level wastes, where conditioning in a cement matrix is an important barrier for nuclide migration. The chemical transformation of \( \alpha \)-ISA was measured as a function of the solid:liquid ratio, temperature and amount of oxygen present in the headspace of the suspensions. For the latter parameter parallel experiments were carried out under laboratory conditions, under argon cover gas and under exclusion of air in a nitrogen-atmosphere glove box.
1.2 Difficulties in the experiments

One crucial point in the interpretation of an observed disappearance of $\alpha$-ISA from solution is the question of whether such an observation may be explained by a chemical transformation or simply by an uptake process onto the solid phase present. In the case of HCP it can be expected (VAN LOON et al., 1997) that, at the high solid to liquid ratios applied in the present experiments, $\alpha$-ISA is almost quantitatively removed from solution by sorption processes. In contrast sorption of $\alpha$-ISA to Ca(OH)$_2$ is rather weak (VAN LOON & GLAUS, 1998; GLAUS & VAN LOON, 2004a). However, relatively large concentrations of $\alpha$-ISA were used in those experiments, and therefore not enough sensitivity for detecting small amounts of sorbed $\alpha$-ISA was achieved. For the purpose of discrimination between chemical transformation and sorption, the formation of transformation products and the concentration of non-purgeable organic carbon (NPOC) was also monitored in the experiments. Although the chemical transformation of $\alpha$-ISA was not understood in terms of a chemical reaction mechanism in the experiments described in GLAUS & VAN LOON (2004a), a series of low-molecular weight carboxylic acids, including glycolate, formate, lactate and acetate turned out to be reliable indicators for chemical transformation of $\alpha$-ISA.

Another problem in these types of experiments lies in possibly slow reaction kinetics of transformation of $\alpha$-ISA and the uncertainty, whether or not the systems have reached an equilibrium state. With respect to the purpose of making reliable predictions for the transformation rates under repository conditions, it is necessary to carry out the experiments at room temperature. From previous tests (not shown) it was known that the reaction rate constants for transformation of $\alpha$-ISA are fairly independent of the initial concentration of $\alpha$-ISA. For this reason it was necessary to carry out the experiments at room temperature at the lowest possible initial concentrations of $\alpha$-ISA. Otherwise only insignificant fractions of $\alpha$-ISA are turned over in a reasonable time. The handling of such low concentrations of $\alpha$-ISA made it necessary to solve several technical problems, such as analytical methods and the storage of samples. A resort from such a situation is to carry out the experiments at elevated temperatures. However, it could already be concluded from previous test experiments (not shown) that the chemical transformation of $\alpha$-ISA comprises a network of reaction steps, probably also involving surface-controlled reaction mechanisms, and that extrapolation from high temperature experiments to ambient temperature may not be unproblematic.
A last remark concerns the term "slow reactions". This term may be interpreted differently depending on the time scales under consideration. In the present context it means that the concentrations of the compound under investigation will change at least by $5 - 10\%$ during time scales of months. However, such changes in concentration can only be monitored, if the analytical accuracy is adequate. The latter point is especially difficult to assess in situations, where results obtained at completely different times have to be compared with each other. A simple variance analysis of calibration curves — as it is often used to assess the accuracy of an analytical technique — is inadequate in such situations. A practical example, which has a direct relation to the subject of the present work, shall illustrate these considerations. Previous work (VAN LOON & GLAUS, 1998) reported data on the chemical stability of filtered solutions of $\alpha$-ISA in an artificial cement pore water. Fig. 1.1 shows these data in a relative representation, in which the concentration of $\alpha$-ISA after a storage time $t$ is divided by its initial concentration at zero time. In view of the error bars it was concluded that $\alpha$-ISA is chemically stable during the time scales investigated. However, on closer scrutiny of the data, a decrease in concentration of $\sim 5\%$ within $\sim 3$ years cannot be excluded. No such statement was made in the cited work, because the decrease was within the range of experimental uncertainty. With respect to the measured $\alpha$-ISA concentrations of $\sim 50$ mM in the cellulose degradation experiments, the possible

![Fig. 1.1: Relative concentration of $\alpha$-ISA in filtered artificial cement pore water solutions obtained from alkaline degradation of cellulose. Time refers to the storage time of the filtered solutions, which were stored under exclusion of air in a glove box. $ISA_0$ is the concentration of $\alpha$-ISA immediately measured after filtering and $ISA_t$ the concentration after storage time $t$.](image-url)
concentration decrease of $\alpha$-ISA would thus be $\sim 2.5$ mM at the maximum on an absolute scale. If the reaction responsible for the possible decrease in $\alpha$-ISA concentration was zero-order with respect to $\alpha$-ISA, an almost quantitative turnover of $\alpha$-ISA would thus be expected for an experiment with an initial $\alpha$-ISA concentration of 2.5 mM within three years. Because such concentrations are by a factor of $>1000$ larger than the detection limit of $\alpha$-ISA, the verification of a quantitative turnover of $\alpha$-ISA would pose no analytical problems in such an experiment.

1.3 Structure of the report

During the project different procedures were applied concerning experimental details in the sense of a "learning procedure". The full experimental material is described in this report in order to document the various developments made as the work progressed and to point out the possible problems. For the sake of easy referencing the individual experiments are labelled in their chronological order. Tab. 1.1 gives an overview of all experiments, the most important conditions under which they were carried out and whether they were used to develop the methodology or whether the results were used for the final conclusions.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Type of solid; Solid-to-liquid ratio (g dm⁻³)</th>
<th>Initial concentrations of α-ISA, [ISA] (mM)</th>
<th>Temperature</th>
<th>Atmosphere</th>
<th>Main observations</th>
<th>Possible issues with methodology</th>
<th>Addressed in experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISA.1001</td>
<td>Ca(OH)₂, 25 / 100</td>
<td>0.5 / 2.5</td>
<td>−25 °C</td>
<td>Argon cover gas</td>
<td>Quantitative transformation of α-ISA. Reaction rate dependent on S/L.</td>
<td>Cover gas not sufficient to exclude the presence of oxygen. Sample storage: NPOC measurements.</td>
<td>ISA.1005, ISA.1011</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N₂, atmosphere glove box</td>
<td>Partial transformation of α-ISA.</td>
<td></td>
<td>ISA.1005, ISA.1011</td>
</tr>
<tr>
<td>ISA.1002</td>
<td>Ca(OH)₂, 100</td>
<td>0.5</td>
<td>−25 °C</td>
<td>Air</td>
<td>Almost same reaction rate under both types of atmosphere</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISA.1003</td>
<td>Ca(OH)₂, 100</td>
<td>0.5</td>
<td>86 °C</td>
<td>Vacuum oven filled with argon</td>
<td>Quantitative transformation of α-ISA</td>
<td>Protective gas not sufficient to exclude the presence of oxygen. NPOC measurements.</td>
<td>ISA.1005, ISA.1007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N₂, atmosphere glove box</td>
<td>Partial transformation of α-ISA.</td>
<td></td>
<td>ISA.1005, ISA.1011</td>
</tr>
<tr>
<td>ISA.1004</td>
<td>Hardened cement paste; 0 / 10 / 400</td>
<td>1.0 / 1.06 / 27</td>
<td>−28 °C</td>
<td>N₂, atmosphere glove box</td>
<td>Partial transformation of α-ISA.</td>
<td>Relatively high background concentrations of reaction products already present in HCP.</td>
<td>Not addressed further, however, not critical for the main conclusions from this experiment</td>
</tr>
<tr>
<td>ISA.1005</td>
<td>Ca(OH)₂, 100</td>
<td>0.05 / 0.10</td>
<td>−28 °C</td>
<td>N₂, atmosphere glove box</td>
<td>Almost quantitative transformation of α-ISA. Turnover of α-ISA can’t be explained by traces of oxygen in the glove box.</td>
<td>Experiment abandoned too early</td>
<td>ISA.1011</td>
</tr>
<tr>
<td>ISA.1006</td>
<td>Ca(OH)₂, 50 / 75 / 100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Abandoned owing to leaking vessels</td>
<td>ISA.1007</td>
</tr>
<tr>
<td>ISA.1007</td>
<td>Ca(OH)₂, 50 / 75 / 100</td>
<td>0.25 / 0.10</td>
<td>90 °C</td>
<td>Oven placed in N₂ atmosphere glove box</td>
<td>Partial transformation of α-ISA. Reaction rate dependent on S/L.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISA.1008</td>
<td>Ca(OH)₂, 50 / 75 / 100</td>
<td>0.25 / 0.10</td>
<td>90 °C</td>
<td>Oven placed in N₂ atmosphere glove box</td>
<td>Addition of fresh Ca(OH)₂ to a reacted suspension reanimates the reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISA.1009</td>
<td>Ca(OH)₂, 100</td>
<td>0.57</td>
<td>−28 °C</td>
<td>N₂ atmosphere glove box</td>
<td>Turnover of α-ISA limited by the amount of oxygen added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISA.1010</td>
<td>Ca(OH)₂, ≈3000 Hardened cement paste; 0−1800</td>
<td>≈5</td>
<td>−28 °C</td>
<td>N₂ atmosphere glove box</td>
<td>≈1 μmol of α-ISA reacted per gram of Ca(OH)₂ or HCP (as a very rough rule of thumb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISA.1011</td>
<td>Ca(OH)₂, 100</td>
<td>0.05 / 0.10</td>
<td>−28 °C</td>
<td>N₂, atmosphere glove box</td>
<td>Partial transformation of α-ISA (28 °C in agreement with results from ISA.1005) at both temperatures</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2 EXPERIMENTAL

Solutions of the lactone of α-ISA in artificial cement pore water were contacted either with Ca(OH)$_2$ or HCP under various aerobic or anaerobic conditions.

The composition of artificial cement pore water (denoted as ACW-I hereafter) was taken from BERNER (1990) and had the following composition: 114 mM Na, 180 mM K, ~2 mM Ca and a pH of 13.3. It was prepared by flushing 1 dm$^3$ of water with argon for ~30 min and adding 4.56 g of NaOH (Merck, 100 %), 11.61 g of KOH (Merck, 87 %) and 10 g of Ca(OH)$_2$ (Merck or Fluka, 100 %). The mixture was left standing for ~24 h, upon which the liquid was filtered off through a 0.45 µm membrane filter (cellulose mixed-ester, Schleicher & Schuell ME25, Germany) after discarding the first 100 cm$^3$. All steps were carried out in a glove box under controlled N$_2$ atmosphere (CO$_2$, O$_2$ < 5 ppm) at a temperature of 28 ± 2 °C.

The lactone form of α-ISA was prepared according to WHISTLER AND BEMILLER (1963) using a modification given in GLAUS et al. (1999). Mixtures of ACW-I and Ca(OH)$_2$ were prepared in 50 cm$^3$ thick-wall PTFE containers (Semadeni, Switzerland) or in polysulfone centrifugation tubes by weighing the solid and adding argon-flushed ACW-I. The reactions were started by adding a suitable stock solution of α-ISA in ACW-I. This method was used for both the preparation of larger batches, from which aliquots were sampled (denoted as "single-batch experiments") after different reaction times, and the preparation of smaller batches (denoted as "multiple-batch experiments"), which were consumed entirely for a single sampling.

Different ways of maintaining anaerobic conditions were applied in the present work. The procedures may not all be regarded as optimum technical solutions, as they depended on the equipment available:

1. Sample preparation, storage of the samples and aliquot sampling in a glove box under controlled N$_2$ atmosphere (CO$_2$, O$_2$ < 5 ppm). This procedure was applied in the beginning of the project to experiments carried out at ambient temperature only (ISA.1001). Later on it was applied to experiments ISA.1004 to ISA.1011.

Merck Ca(OH)$_2$ was used for experiments ISA.1001 – ISA.1005, whereas Fluka Ca(OH)$_2$ was used in the forthcoming experiments ISA.1007 – ISA.1009. In experiments ISA.1010 and ISA.1011 the two products were tested in a cross-comparison. No difference in terms of reactivity of α-ISA was found thereby.
2. Preparation of stock solutions and suspensions was carried out in the glove box. Closed suspensions were brought to laboratory atmosphere where the vessels were opened to add a concentrated solution of \( \alpha \)-ISA. The suspensions were flushed with argon during that time. Storage of samples and aliquot sampling was carried out under argon cover gas. On each opening of the vessels the suspensions were flushed for 3 min with argon. This procedure was applied to part of the experiments carried out at room temperature and at 90 °C (ISA.1001). A minimal contact of the reaction systems with air could thereby not be excluded and it is not possible to specify a maximum possible concentration of \( O_2 \) in these experiments. Because significant differences in the reaction behaviour of \( \alpha \)-ISA occurred between experiments carried out according to the first and this procedure, this second procedure was abandoned.

3. Sample preparation in a glove box under controlled \( N_2 \) atmosphere (\( CO_2, O_2 < 5 \) ppm) in PTFE containers. Sample storage at high temperatures was realised in a vacuum oven filled with argon as the inert gas (ISA.1003). For aliquot sampling, the vessels were transferred to a glove box and then returned to the vacuum oven. The momentary drop in temperature is regarded as insignificant for the course of the transformation reaction.

4. Use of an oven in the glove box under controlled \( N_2 \) atmosphere (\( CO_2, O_2 < 5 \) ppm). This was the best methodology for avoiding contact of \( O_2 \) with the experimental systems at elevated temperature (ISA.1007, ISA.1008). The leakage rate of the PTFE containers increased significantly at temperatures of \( \sim 90 \) °C as compared to room temperature, most probably because of the flow characteristics of the material.

For the analysis of organic compounds present in the solution phase, aliquots of these mixtures were taken after a given contact time under flushing with argon gas and filtered through 0.2 \( \mu m \) membrane filters (nylon filters, type Uniflo, Schleicher & Schuell, Germany), while discarding the first millilitre. In a few cases, the remaining solid was subjected to analysis of possibly sorbed organic species. For this purpose, the solid was washed with a minimum of water to remove undesired solution species and then dissolved in 1 M HCl.

The high performance anion exchange chromatography (HPAEC) system (DX-500, Dionex, Switzerland) using a CarboPac PA-100\(^\circ\) column (Dionex, Switzerland) to measure the concentrations of \( \alpha \)-ISA has been described elsewhere (GLAUS et al.,
Samples of α-ISA in ACW-I were diluted with water by a factor of at least 10, in order to avoid matrix effects caused by large hydroxide concentrations present in the samples injected. Samples that could not be diluted to such values were pre-treated first with Onguard-H® cartridges in the H⁺ form (Dionex, Switzerland).

A similar high performance ion exclusion chromatography (HPIEC) system as described in GLAUS et al. (1999) was used for the analysis of short-chain aliphatic carboxylic acids. It consists of a DX-600 chromatograph (Dionex, Switzerland) equipped with a 9x250 mm IonPac ICE-AS6® column (Dionex, Switzerland) and a conductivity detector combined with an AMMS-ICE anion exclusion micromembrane suppressor. Samples were injected from a 50 µl loop and eluted at a flow of 1 cm³ min⁻¹ at 50 °C using 0.4 mM heptafluorobutyric acid as the eluent and 5 mM tetrabutylammonium hydroxide as the suppressor regenerant. Various test experiments and previous investigations (GLAUS et al., 1999) have shown that these conditions are best suited to analyse short-chain aliphatic acids in the presence of larger concentrations of α-ISA. The latter compound elutes as the lactone form under these conditions and is detected only as a broad bump with very low sensitivity, whereas the peaks of the short-chain aliphatic carboxylic acids remain clearly identifiable.

The separation principle in HPIEC is the Donnan exclusion of anions owing to the presence of micropores with a high degree of fixed negative charges. This causes the anions to be eluted in the void volume, whereas uncharged molecules may distribute in the micropores leading to a retarded elution. Additionally, separation is effectuated by interaction with the stationary phase, particularly by (FISCHER, 2002):

- Hydrophobic interactions: This leads to a strong retention of typically fatty acids.

- Polar interactions mainly taking place by hydrogen bonding. This leads to a differentiation between various types of hydroxycarboxylic acids, which is of high importance in the present context.

- π-π electron interactions, being of importance in the case of aromatic carboxylic acids.

---

3 If the analysis is performed at ambient temperature, α-ISA elutes mainly as the open-chain form, thus strongly interfering with other carboxylic acids.
Finally a few test measurements for the presence of dissociated organic acids were carried out using high performance anion exchange chromatography with conductometric detection (HPAEC-cond). For that purpose the Dionex DX-600 system was equipped with a 4x250 mm IonPac AS16® column (Dionex, Switzerland). Elution of the analytes was monitored by conductivity after neutralisation of the eluent ions by an ASRS Ultra micromembrane suppressor working in the autosuppression mode.

The concentration of total non-purgeable dissolved organic carbon (NPOC) was analysed by a TOC-V WP® device (Shimadzu, Reinach, Switzerland) using UV-promoted persulfate wet oxidation. The oxidation reagent was a 10.5 % solution of Na$_2$S$_2$O$_8$ in 3.8 % H$_3$PO$_4$. Calibrations were performed with solutions of potassium hydrogenephthalate as a standard. Alkaline samples were acidified using a suitable amount of ~20 %H$_3$PO$_4$ before analysis.

The treatment of experimental uncertainty is crucial for the discussion of the results in this report, because it determines the limits, upon which a decrease of $\alpha$-ISA concentration may be taxed as significant or not. The procedure to quantify the experimental uncertainties follows the recommendations given by the EURACHEM Working Group on Uncertainty in Analytical Measurements (WILLIAMS et al., 1995), which is virtually a practical application for analytical chemistry of the recommendations given in the "ISO-Guide" (N.N., 1993). The procedure allows for an integrative treatment of statistical and non-statistical (systematic) errors and briefly consists of the following steps:

1. Identification and specification of the different sources of uncertainty

2. Quantification of the uncertainty increments

3. Calculation of a "combined uncertainty" in the result

4. Re-evaluation of the uncertainty increments and recalculation of the combined uncertainty (if necessary)

It would be beyond the scope of this report to trace back the calculation of experimental uncertainties in detail. Just as a guideline, it may be mentioned that the uncertainties of analytical results both obtained for HPAEC and NPOC measurements were mainly based on the transformation of signal to concentration using linear calibration functions. Systematic errors were formally allocated to the calibration data in order to be properly included in the evaluation (GLAUS, 2001).
The estimation of experimental uncertainties is always dependent on a model comprising a list of the sources for experimental uncertainty involved and a procedure for how these individual uncertainties can be compounded to an overall experimental uncertainty of an analytical result or a thermodynamic or kinetic constant. Also, in the present set of data, there are cases which give the feeling that the experimental uncertainty calculated may underestimate the true uncertainty. However, there is no better to address this issue, and the uncertainties specified are at least useful for comparative purposes, i.e. they may reveal whether a given analytical result has been obtained in an ideal range or at the limits of the “analytical window”.

3 EXPERIMENT ISA.1001 — Ca(OH)$_2$, 25 °C, various pre-tests

3.1 Experimental

The chemical transformation of $\alpha$-ISA in the presence of Ca(OH)$_2$ (Merck) as the solid phase was studied in this experiment at ambient temperature under various conditions. Tab. 3.1 gives an overview of the various reaction conditions tested.

The exclusion of air by argon-flushing was tested in view of the experiments to be conducted at higher temperatures, such as 90 °C. When the experiments were started it was not clear whether it would be possible to introduce an oven at that temperature into a glove box and a vacuum oven was not available. The variation of different materials for the reaction vessels was simply chosen for logistic reasons. The variation of the initial concentration of $\alpha$-ISA was based on the consideration that this determines the time window for the experiment, which was not known from the beginning. In addition, reference systems containing $\alpha$-ISA, but no Ca(OH)$_2$ were set up later during the course of this project.

In this experiment, aliquot-samples were taken from the previously homogenised suspensions for analysis. No special precaution was taken to prevent further chemical reactions in the filtered samples, with the exception that the samples were stored in a refrigerator at ~4 °C. Such a procedure has proven of value during previous experiments (VAN LOON & GLAUS, 1998). However, in the present work, this procedure turned out to be insufficient. It was observed that the concentration of $\alpha$-ISA slowly
decreased in glass vials when storing the samples for a couple of weeks. The reason for this unexpected behaviour may be found in the alkaline attack of the glass surface by ACW-I and subsequent sorption of \( \alpha \)-ISA on the precipitates formed. In contrast to previous work (VAN LOON & GLAUS, 1998), the \( \alpha \)-ISA concentrations were very low (order of a tens to hundreds of micromolar in contrast to order of tens of millimolar), and thus the samples may be more susceptible to such artefacts.

### Tab. 3.1: Overview of the experimental conditions tested in experiment ISA.1001.

[\( \text{[ISA]}_n \)] is the initial concentration of \( \alpha \)-ISA added\(^a\) to the experiments.

<table>
<thead>
<tr>
<th></th>
<th>PTFE</th>
<th>Polysulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Argon-flushing</td>
<td>Glove box (( \text{N}_2 ))</td>
</tr>
<tr>
<td>( \text{Ca(OH)}_2 ) (g dm(^{-3}))</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>( \text{[ISA]}_n ) (^b)</td>
<td>0 / 0</td>
<td>0 / 0</td>
</tr>
<tr>
<td>( \text{[ISA]}_n ) (^b)</td>
<td>0.5 / 3.0</td>
<td>0.5 / 3.0</td>
</tr>
<tr>
<td>( \text{[ISA]}_n ) (^b)</td>
<td>2.5 / 15</td>
<td>2.5 / 15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<td>100</td>
</tr>
<tr>
<td>( \text{[ISA]}_n ) (^b)</td>
<td>0 / 0</td>
<td>0 / 0</td>
</tr>
<tr>
<td>( \text{[ISA]}_n ) (^b)</td>
<td>0.5 / 3.0</td>
<td>0.5 / 3.0</td>
</tr>
<tr>
<td>( \text{[ISA]}_n ) (^b)</td>
<td>2.5 / 15</td>
<td>2.5 / 15</td>
</tr>
</tbody>
</table>

\(^a\) Added as the lactone form; the solution volume was 30 cm\(^3\)

\(^b\) First number given as mM \( \alpha \)-ISA, second number given as mM C (carbon)

### 3.2 Results and discussion

An overview of the full data obtained is shown in terms of concentrations of \( \alpha \)-ISA and sum of reaction products as a function of reaction time for the experiments carried out in PTFE containers in Fig. 3.1a and those in polysulfone tubes in Fig. 3.1b. The data
were corrected for background concentrations found in blank experiments containing only Ca(OH)$_2$ and ACW-I. In almost all cases the net concentrations of low-molecular weight carboxylic acids exceeded these background values by a factor of at least ~5. This shows that the increase in concentration of these compounds has to be regarded as significant. The results of the experiments carried out in polysulfone tubes in the glove box were further corrected for evaporation of water. Although the weights of the containers were not monitored, evaporation of water could clearly be demonstrated using the results of ion-chromatographic measurements of the concentrations of Na$^+$ and K$^+$ in the samples (data not shown). These results demonstrated that water loss was only significant in the mentioned case. PTFE containers turned out to be leak-proof, and water loss from polysulfone tubes stored under laboratory atmosphere was negligible owing to the humid atmosphere.

Figs. 3.1a and b show that the extent of transformation of $\alpha$-ISA is almost complete in the experiments kept under argon-flushing, whereas only small amounts of $\alpha$-ISA reacted in the systems kept in the glove box. In both systems the formation of low-molecular carboxylic acid shows the disappearance of $\alpha$-ISA can be explained at least in part by a chemical transformation and not simply by sorption to the solid$^4$. Tab. 3.2 shows a mass balance for carbon based on the decrease of $\alpha$-ISA concentration as compared to the concentration of identified reaction products. The amount of carboxylic acids formed, i.e. glycolate, formate and acetate, is of the order of 40% of the amount of $\alpha$-ISA totally reacted throughout.

---

$^4$ The results of carbon measurements further supported this conclusion and showed that the fraction of $\alpha$-ISA chemically transformed largely exceeded the amount of $\alpha$-ISA possibly sorbed to the solid (cf Tabs. 3.3 and 3.4.)
Fig. 3.1a: Overview of reactivity of α-ISA in Ca(OH)\textsubscript{2}/ACW-I suspensions at 22 ±2 °C carried out in PTFE containers.
Fig. 3.1b: Overview of reactivity of α-ISA in Ca(OH)$_2$/ACW-I suspensions at 22 ±2 °C carried out in polysulfone tubes.
**Tab. 3.2:** Carbon mass balance in experiments ISA.1001 after a reaction time of ~240 days: The first number indicates the amount of carbon corresponding to the loss of α-ISA from solution; the second number the summary amount carbon given by the reaction products identified (both given as mM C) a.

<table>
<thead>
<tr>
<th>Vessel material</th>
<th>PTFE</th>
<th>Glove box (N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exclusion of air</td>
<td>Argon-flushing</td>
<td>Ca(OH)₂ (g dm⁻³)</td>
</tr>
<tr>
<td>[ISA]₀: 3.0 b</td>
<td>3.0 / 1.3</td>
<td>3.0 / 1.4</td>
</tr>
<tr>
<td>[ISA]₀: 15 b</td>
<td>5.9 / 1.3</td>
<td>15.0 / 5.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vessel material</th>
<th>Polysulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exclusion of air</td>
<td>Argon-flushing</td>
</tr>
<tr>
<td>[ISA]₀: 3.0 b</td>
<td>3.0 / 1.5</td>
</tr>
<tr>
<td>[ISA]₀: 15 b</td>
<td>4.2 / 1.5 ± 1.0</td>
</tr>
</tbody>
</table>

a Some scatter of the data has been observed in cases where the extent of transformation of α-ISA reached a constant value. The scatter is given only for those cases where it clearly exceeded 10 %.

b Concentration of α-ISA initially added: mM C
Regardless of the problems with storage of the samples, a few other conclusions may be drawn from the results.

**Conclusion #1 (cf. Fig. 3.2):**

In an initial phase, the chemical transformation of $\alpha$-ISA proceeds at similar rate in argon-flushed vessels and in parallel experiments carried out in the glove box. However the reaction in the latter experiments was stopped by unknown reasons. One may speculate that traces of oxygen may be responsible for the initially observed reactivity of $\alpha$-ISA in the glove box experiments. However, such phenomena were also observed in later experiments, where rigorous experimental procedures (such as the "acclimatisation of chemicals" to the glove box atmosphere) made rather implausible the presence of such "large amounts" of oxygen, as required for the observed extent of $\alpha$-ISA reaction, in the reaction vessels.

**Fig. 3.2:**

Influence of atmosphere on transformation of $\alpha$-ISA.

$Ca(OH)_2$ (Merck): 100 g dm$^{-3}$

$[ISA]_i$: 0.5 mM (3.0 mM C)

22 ± 2°C

PTFE vessels

Single-batch

Atmosphere: s. legend
Conclusion #2 (cf. Fig. 3.3):

The initial reaction rate for the chemical transformation of \( \alpha \)-ISA depends (possibly linearly) on the amount of Ca(OH)\(_2\) present.

![Figure 3.3: Influence of solid:liquid ratio on transformation of \( \alpha \)-ISA.](image)

\[\text{Ca(OH)}_2\ (\text{Merck}): \text{s. legend} \]
\[\text{[ISA]}_0: 2.5 \text{ mM (15 mM C)} \]
\[22 \pm 2^\circ\text{C} \]
\[\text{Vessel type: polysulfone} \]
\[\text{Single-batch} \]
\[\text{Laboratory, Argon-flush} \]

Conclusion #3 (cf. Fig. 3.4):

The material of the vessel has no impact on the reaction rate.

![Figure 3.4: Influence of vessel material on transformation of \( \alpha \)-ISA.](image)

\[\text{Ca(OH)}_2\ (\text{Merck}): 100 \text{ g dm}^{-3} \]
\[\text{[ISA]}_0: 2.5 \text{ mM (15 mM C)} \]
\[22 \pm 2^\circ\text{C} \]
\[\text{Vessel type: varied} \]
\[\text{Single-batch} \]
\[\text{Laboratory, Argon-flush} \]
Conclusion #4 (cf. Fig. 3.5 and Fig. 3.6):

The initial reaction rate constant does not depend on the concentration of α-ISA. In a first approximation the reaction can be described by a zero-order reaction law (Fig. 3.5). However, it may possibly turn into first-order at low concentrations of α-ISA as is illustrated by Fig. 3.6.

Fig. 3.5:
Influence of initial concentration on transformation of α-ISA.
Ca(OH)$_2$ (Merck):
100 g dm$^{-3}$
[ISA]$_{in}$: varied
22 ± 2°C
Vessel type: polysulfone
Single-batch
Laboratory, Argon-flush

Fig. 3.6:
Logarithmic representation of the data shown in Fig. 3.5.
Conclusion #5 (cf. Fig. 3.7, Tabs 3.3 and 3.4):

The concentration of $\alpha$-ISA measured after 1 day of reaction is generally lower than the concentration initially added to the experiments. Part of $\alpha$-ISA is thus rapidly lost. Fig. 3.7 shows that the amount of $\alpha$-ISA sorbed depends on the amount of $\text{Ca(OH)}_2$ present in the experiment, which might suggest that the loss of $\alpha$-ISA may be explained by a sorption process. However, as demonstrated by Figs. 3.1a and 3.1b the concentrations of reaction products formed within the first 24 h is rather low. This points to an interpretation which includes both sorption processes and chemical transformation taking place in the initial reaction phase. However the resolution of the data does not allow for a discrimination between these processes to be made.\(^5\)

\(^5\) Note that it is shown in forthcoming experiments, in which the reliability of measurement of the reaction products and of NPOC was much better, it definitely turned out that the loss of $\alpha$-ISA from solution is mainly explained by a chemical transformation reaction and not by sorption.
The involvement of chemical transformation processes in the further phase of reaction is partly underlined by the measurements of NPOC in the solution phase, which remained rather constant (cf. Tab. 3.3 for experiments with an initial \(\alpha\)-ISA concentration of 0.5 mM and Tab. 3.4 for experiments with an initial \(\alpha\)-ISA concentration of 2.5 mM). It has to be noted that the carbon measurements were, at that stage of the project, affected by some unknown bias of the results (possibly by the use of a new type of sample vessels).

**Tab. 3.3:** NPOC (mg dm\(^{-3}\) C) measured as a function of time in filtrates of experiments carried out with \([ISA]_0 = 0.5\) mM (corresponding to 36 mg dm\(^{-3}\) C). All values are corrected for blanks containing Ca(OH)\(_2\), but no \(\alpha\)-ISA. No correction for changes in volume due to evaporation of water has been applied. Experimental uncertainties only refer to the analytical measurements, they do not include possible contamination by carbon.

<table>
<thead>
<tr>
<th>Vessel material</th>
<th>PTFE</th>
<th></th>
<th>Polysulfone</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Exclusion of air</td>
<td>Argon-flushing</td>
<td>Glove box (N(_2))</td>
<td>Argon-flushing</td>
<td>Glove box (N(_2))</td>
</tr>
<tr>
<td>(\text{Ca(OH)}_2) (g dm(^{-3}))</td>
<td>25</td>
<td>100</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>Reaction time (d)</td>
<td>1</td>
<td>43.0 ± 2.0</td>
<td>n.d.</td>
<td>37.0 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>40(^a) / 29(^b)</td>
<td>30.0 ± 1.1</td>
<td>23.0 ± 0.7</td>
<td>37.0 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>81(^a) / 83(^b)</td>
<td>24.9 ± 1.0</td>
<td>23.2 ± 0.9</td>
<td>32.4 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>131</td>
<td>28.2 ± 0.7</td>
<td>26.1 ± 0.6</td>
<td>34.3 ± 0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vessel material</th>
<th>Polysulfone</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>Exclusion of air</td>
<td>Argon-flushing</td>
<td>Glove box (N(_2))</td>
<td>Argon-flushing</td>
</tr>
<tr>
<td>(\text{Ca(OH)}_2) (g dm(^{-3}))</td>
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<td>100</td>
<td>25</td>
</tr>
<tr>
<td>Reaction time (d)</td>
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<td>33.0 ± 1.6</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>40(^a) / 29(^b)</td>
<td>28.0 ± 1.2</td>
<td>18.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>81(^a) / 83(^b)</td>
<td>26.5 ± 1.1</td>
<td>25.4 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>131</td>
<td>22.9 ± 0.5</td>
<td>22.6 ± 0.6</td>
</tr>
</tbody>
</table>

\(a\) For experiments with 25 g dm\(^{-3}\) of Ca(OH)\(_2\)  \(b\) For experiments with 100 g dm\(^{-3}\) of Ca(OH)\(_2\)  \(c\) Not determined
Some of the results indicate even larger carbon concentrations than those due to added $\alpha$-ISA. The results in Tabs 3.3 and 3.4 are shown for the sake of completeness. A detailed interpretation of the data is not possible; the reader is referred to the results of the forthcoming experiments (e.g. ISA.1005 and ISA.1007), where the accuracy of the NPOC measurements was much better.

**Tab. 3.4:** NPOC (mg dm$^{-3}$ C) measured as a function of time in filtrates of experiments carried out with [ISA]$_0$ = 2.5 mM (corresponding to 180 mg dm$^{-3}$ C). All values are corrected for blanks containing Ca(OH)$_2$, but no $\alpha$-ISA. No correction for changes in volume due to evaporation of water has been applied. Experimental uncertainties only refer to the analytical measurements, they do not comprise possible contaminations by carbon.

<table>
<thead>
<tr>
<th>Vessel</th>
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<th>Glove box (N$_2$)</th>
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<tr>
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<td>25</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>Reaction time (d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>172.0 ± 10.8</td>
<td>141.0 ± 7.7</td>
<td>173.0 ± 10.8</td>
</tr>
<tr>
<td>40$^a$ / 29$^b$</td>
<td></td>
<td>170.0 ± 9.4</td>
<td>137.0 ± 9.9</td>
<td>174.0 ± 9.3</td>
</tr>
<tr>
<td>81$^a$ / 83$^b$</td>
<td></td>
<td>169.6 ± 11.5</td>
<td>131.3 ± 6.9</td>
<td>176.3 ± 12.4</td>
</tr>
<tr>
<td>131</td>
<td></td>
<td>165.4 ± 6.8</td>
<td>117.9 ± 3.7</td>
<td>173.9 ± 7.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Polysulfone</th>
<th>Exclusion of air</th>
<th>Argon-flushing</th>
<th>Glove box (N$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$ (g dm$^{-3}$)</td>
<td></td>
<td>25</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>Reaction time (d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>191.0 ± 12.9</td>
<td>144.0 ± 8.0</td>
<td>196.0 ± 13.1</td>
</tr>
<tr>
<td>40$^a$ / 29$^b$</td>
<td></td>
<td>165.0 ± 14.6</td>
<td>137.0 ± 6.8</td>
<td>168.0 ± 15.9</td>
</tr>
<tr>
<td>81$^a$ / 83$^b$</td>
<td></td>
<td>176.4 ± 12.4</td>
<td>144.5 ± 8.3</td>
<td>181.8 ± 13.2</td>
</tr>
<tr>
<td>131</td>
<td></td>
<td>183.3 ± 8.0</td>
<td>125.1 ± 4.3</td>
<td>188.0 ± 8.3</td>
</tr>
</tbody>
</table>

$^a$ For experiments with 25 g dm$^{-3}$ of Ca(OH)$_2$  
$^b$ For experiments with 100 g dm$^{-3}$ of Ca(OH)$_2$
Conclusion #6 (cf. Tab. 3.5, Figs. 3.8a–d, 3.9):

Glycolate, formate, lactate and acetate are main reaction products obtained from the chemical transformation of α-ISA, as is illustrated by the HPIEC chromatograms shown in Figs. 3.8a–d. Fig. 3.9 shows exemplarily the evolution of reaction products as a function of time.

**Fig. 3.8a:** HPIEC chromatograms of filtrates from an experiment to which no α-ISA was added. The experiment was carried out in PTFE containers at 100 g dm$^{-3}$ of Ca(OH)$_2$ under argon-flushed atmosphere. The legend indicates the reaction time and sample dilution.
Fig. 3.8b: HPIEC chromatograms of filtrates from an experiment with $[\alpha$-ISA]$_n$ = 2.5 mM. The experiment was carried out at 100 g dm$^{-3}$ of Ca(OH)$_2$ under argon-flushed atmosphere. The peak measured at 17 min. is carbonate. The legend indicates the reaction time and sample dilution.

Fig. 3.8c: HPIEC chromatograms of filtrates from an experiment to which no $\alpha$-ISA was added. The experiment was carried out in PTFE containers at 100 g dm$^{-3}$ of Ca(OH)$_2$ under glove box atmosphere. The legend indicates the reaction time and sample dilution.
Fig. 3.8d: HPIEC chromatograms of filtrates from an experiment with [α-ISA]_n = 2.5 mM. The experiment was carried out at 100 g dm⁻³ of Ca(OH)_2 under glove box atmosphere. The legend indicates the reaction time and sample dilution.

The identification of reaction products is on a relatively reliable basis. In view of the principles pointed out in section 2 on the analyte separation by HPIEC, it can be understood that acidic compounds are retained in HPIEC only, if they are partly present as undissociated neutral molecules under the conditions of the eluent. Variation of the eluent concentration may thus have an impact on the retention time provided that the logarithmic dissociation constant of the acid lies within the same order of magnitude as the pH of the eluent. It has further been shown that different acids respond differently on variations of temperature. For this reason the identification of unknown peaks will be more reliable, if tested under various eluent concentrations and temperatures. Tab. 3.5 gives an overview of the elution behaviour of various carboxylic and inorganic acids at various conditions tested in the frame of the present work.

---

6 Undissociable organic compounds like aliphatic alcohols are thus not detected in HPIEC.
Tab. 3.5: Overview of retention times of various organic and inorganic weak acids at different elution conditions.

<table>
<thead>
<tr>
<th></th>
<th>0.4mM HFBA a</th>
<th>0.4mM HFBA</th>
<th>1.6mM HFBA</th>
<th>1.6mM HFBA</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>20° C</td>
<td>50° C</td>
<td>20° C</td>
<td>50° C</td>
</tr>
<tr>
<td>Oxalate</td>
<td>n.m. b</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>Maleate</td>
<td>6.56</td>
<td>5.28</td>
<td>n.d. c</td>
<td>n.d.</td>
</tr>
<tr>
<td>Tartrate</td>
<td>7.45</td>
<td>5.90</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>n.d.</td>
<td>~6.0</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Citrate</td>
<td>6.95</td>
<td>6.28</td>
<td>9.0</td>
<td>7.71</td>
</tr>
<tr>
<td>Fluoride</td>
<td>6.7</td>
<td>7.22</td>
<td>8.34</td>
<td>8.73</td>
</tr>
<tr>
<td>Threonate</td>
<td>7.40</td>
<td>7.23</td>
<td>8.41</td>
<td>8.21</td>
</tr>
<tr>
<td>Malate</td>
<td>8.1</td>
<td>7.44</td>
<td>9.87</td>
<td>8.84</td>
</tr>
<tr>
<td>Glycerate</td>
<td>n.d.</td>
<td>7.95</td>
<td>9.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>Glycolate</td>
<td>9.48</td>
<td>9.06</td>
<td>10.67</td>
<td>10.15</td>
</tr>
<tr>
<td>Borate</td>
<td>9.52</td>
<td>9.29</td>
<td>9.51</td>
<td>9.29</td>
</tr>
<tr>
<td>Formate</td>
<td>10.43</td>
<td>9.86</td>
<td>12.19</td>
<td>11.39</td>
</tr>
<tr>
<td>Lactate</td>
<td>11.08</td>
<td>10.56</td>
<td>12.57</td>
<td>11.8</td>
</tr>
<tr>
<td>Succinate</td>
<td>16.90</td>
<td>12.97</td>
<td>18.36</td>
<td>13.96</td>
</tr>
<tr>
<td>Acetate</td>
<td>15.71</td>
<td>14.12</td>
<td>16.12</td>
<td>14.4</td>
</tr>
</tbody>
</table>

a Abbreviation for heptafluorobutyric acid.
b Not measurable: Oxalate elutes together with other anions in the void volume, because of the acidic pK.
c Not determined

As can be seen from Tab. 3.5 various compounds co-elute at the conditions used for separation (0.4 mM HFBA, 50 °C). Through measurement at different elution conditions it was shown unequivocally that, among the peaks in question, threonate was not a reaction product of the chemical transformation of α-ISA. The peak was clearly identified as fluoride, probably being leached from the Ca(OH)₂. From these tests, glycolate, formate, lactate and acetate were among the reaction products. All other acids listed in Tab. 3.5 can be excluded. An exception is oxalate which was detected in HPAEC as the only strongly dissociating acid present in the reaction mixture. Its concentration was, however, so low that the mass balance for identified reaction products was changed within less than 2 %. For this reason oxalate is not specifically included in the mass balances shown in this report. Through cross-comparison with literature data the list of excludable acids could even be prolonged. However this is
outside the scope of the present discussion. It may simply be noted that no significant peaks other than those mentioned were present in the reaction mixtures. The structure of the chromatograms was noticeably more simple than observed for solutions coming from cellulose degradation experiments (GLAUS & VAN LOON, 2004a), where many more peaks corresponding to species with retention times between those of fluoride and glycolate were observed.

![Figure 3.9](image-url)

Fig. 3.9: Concentration of α-ISA and reaction products as a function of time. The fit curves are just shown to guide the eye and do not have any chemical significance.

Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$
[ISA]$_0$: 2.5 mM (15 mM C)
22 ± 2°C
Polysulfone vessels
Single-batch
Laboratory, Argon-flush
4 EXPERIMENT ISA.1002 — Ca(OH)$_2$, 25 °C, test air atmosphere

The aim of this experiment is to compare the reaction rate of experiments carried out under laboratory atmosphere in the presence of oxygen to those carried out under an argon-flushed atmosphere in ISA.1001.

4.1 Experimental

The chemical transformation of $\alpha$-ISA in the presence of 100 g dm$^{-3}$ Ca(OH)$_2$ as the solid phase was studied in polysulfone centrifugation tubes in the same way as in experiment ISA.1001, with the exception that the reaction was studied under air atmosphere instead of argon. Further all samples that could not immediately be analysed, were stored in polyethylene tubes at $-20$ °C. The reaction was followed in three replicate samples.

4.2 Results and discussion

The results, expressed as average values over the three replicate samples, are shown in Fig. 4.1. Also shown in this figure is a comparison to the chemical transformation of $\alpha$-ISA studied under argon-flushed atmosphere (cf. Experiment ISA.1001). Although there seem to be some minor differences between the results obtained under these different conditions, the reaction rate constants and the reaction rate law seem to be very similar.

![Graph showing the influence of atmosphere on transformation of $\alpha$-ISA.](image)

**Fig. 4.1:** Influence of atmosphere on transformation of $\alpha$-ISA.

Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$ $[\text{ISA}]_0$: 0.5 mM (3.0 mM C) 22 ± 2°C
Vessel: s. legend
Single-batch
Atmosphere: Argon-flush for ISA.1001; air for ISA.1002
5 EXPERIMENT ISA.1003 — Ca(OH)$_2$, 28/86 °C, test atmosphere and initial concentration $\alpha$-ISA

5.1 Aim and experimental

The chemical transformation of $\alpha$-ISA in the presence of 100 g dm$^{-3}$ Ca(OH)$_2$ as the solid phase was studied under two conditions:

- At elevated temperature (86 ±2 °C) in PTFE containers using an argon-filled vacuum oven to maintain an O$_2$-free atmosphere. All solutions and the reaction mixtures for these experiments were prepared in a glove box. The closed PTFE containers were then brought to the vacuum oven, where the argon atmosphere was generated by repeatedly evacuating the oven and filling with argon gas. A series of replicate reaction mixtures that were consumed entirely for sampling were prepared for one experiment. It was assumed that access by O$_2$ to the experiments can be prevented as effectively by this procedure, as if the experiments were carried out in a glove box. The initial concentration of $\alpha$-ISA, added as the lactone form, was 0.5 mM (or 3.0 mM C).

- At ambient temperature (~26 ±3 °C) in polysulfone centrifugation tubes. All solutions and the reaction mixtures for these experiments were prepared and kept in a glove box. This experiment is virtually a recurrence of some of the experiments performed under ‘ISA.1001’. Two initial concentrations of $\alpha$-ISA, added as the lactone form, were tested in the present experiment, viz. 0.5 and 0.05 mM (or 3.0 and 0.30 mM C).

For both types of experiments reference experiments containing either $\alpha$-ISA, but no Ca(OH)$_2$, or Ca(OH)$_2$, but no $\alpha$-ISA, were also set up. All samples that could not be analysed immediately, were stored in polyethylene tubes at −20°C in a refrigerator.
5.2 Results and discussion

5.2.1 Experiments at 86 °C

The concentration of α-ISA, of the possible reaction products and their sum are plotted in Fig. 5.1. The data are corrected for background concentrations of the analytes found in the blank systems containing Ca(OH)$_2$, but no α-ISA. As an example, the content of glycolate in the blank system at 102 d was 1 % of the content in the corresponding reaction system, formate was 6 %, lactate was 3 % and acetate was 20 %. All data are corrected for loss of water caused by evaporation during storage in the oven. With exception of one sample, the correction factors are between 1 and 1.05. The data contain some inconsistencies with respect to the transformation rate of α-ISA. In a few reaction systems the transformation of α-ISA proceeded faster than in others. The reason for this behaviour is not known. However, these data suggest that after ~50 days of the reaction the transformation of α-ISA to reaction products is complete.

Fig. 5.1: Concentration of α-ISA and reaction products as a function of time. The fit curves are just shown to guide the eye and do not have any chemical significance.
Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$
[ISA]$_0$: 0.5 mM (3.0 mM C)
86 ± 2°C
PTFE containers
Multiple-batch
Argon-flushed vacuum oven.
5.2.2 Experiments at ambient temperature

The concentrations of $\alpha$-ISA, the possible reaction products and their sum are plotted in Fig. 5.2 and 5.3. The data are corrected for background concentrations of the analytes found in the blank systems containing Ca(OH)$_2$, but no $\alpha$-ISA. All data are further corrected for loss of water caused by evaporation during storage in the glove box.

Fig. 5.2: Concentration of $\alpha$-ISA and reaction products as a function of time. The fit curves are just shown to guide the eye and do not have any chemical significance.
Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$
[ISA]$_{in}$: 0.5 mM (3.0 mM C)
26 ± 3°C
Polysulfone tubes
Multiple-batch
Glove box (N$_2$)

Fig. 5.3: Concentration of $\alpha$-ISA and reaction products as a function of time. The fit curves are just shown to guide the eye and do not have any chemical significance.
Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$
[ISA]$_{in}$: 0.05 mM (0.3 mM C)
26 ± 3°C
Polysulfone tubes
Multiple-batch
Glove box (N$_2$)
In the reference experiments containing the same initial concentration of α-ISA, but no Ca(OH)$_2$, the α-ISA concentration remained constant throughout the same observation time, and none of the transformation products could be detected in significant amounts. Both Figs 5.2 and 5.3 indicate that at least half of the amount of α-ISA lost from solution is transformed to degradation products and does not get sorbed. These findings are thus in agreement to those found in the experiments under ISA.1001 also carried out in the glove box. However the statistical significance of the results in ISA.1003 are more robust in that each of the time points is obtained from separate experiments, whereas all the experimental points in ISA.1001 were obtained from the same experiment. Experiments of the type as shown in Fig. 5.3 seem to be suited to measure the reaction rate constant for transformation of α-ISA in a reasonable time. However, care must be taken in order to keep the measurements within a reasonable analytical window, and that it is possible to discern chemical transformation from sorption processes. The error bars in Fig. 5.3 clearly show that this experiments has been carried out at the lower limit of the analytical window. Especially the measurement of NPOC is problematic with respect to relatively high background values found in the reference systems and to the limited amount of sample available for these measurements. However, by using an improved experimental setup, this situation could certainly be ameliorated. The formation of inorganic carbon can't be measured, since almost all of the carbonate possibly formed will be precipitated as CaCO$_3$.

5.2.3 HPIEC chromatograms

Figs. 5.4 to 5.6 show HPIEC chromatograms of filtrates of experiments reacted for ~100 d. The patterns of product distribution are similar with each other and the ones found in experiments ISA.1001, indicating that the same reaction pathways are used for the chemical transformation of α-ISA at ambient temperature and at elevated temperature. No significant changes in the HPAEC chromatograms, with exception of the decrease of the α-ISA peak, can be observed with increasing reaction time. This suggests that no condensation reactions leading to larger polyhydroxy compounds are actually taking place. Note that no direct quantitative comparison is possible in these figures, because the dilution factors of the samples are not identical.
Fig. 5.4: HPIEC chromatograms of filtrates sampled after 138 d from experiments carried out at 86 °C under argon atmosphere (vacuum oven). The legend indicates the initial experiment composition and the dilution factors of the HPIEC samples.

Fig. 5.5: HPIEC chromatograms of filtrates sampled after 138 d from experiments carried out at ambient temperature in an N₂-atmosphere glove box. The legend indicates the initial experiment composition and the dilution factors of the HPIEC samples.
Fig. 5.6: HPIEC chromatograms of filtrates sampled after 102 d from experiments carried out at ambient temperature in an N₂-atmosphere glove box. The legend indicates the initial experiment composition and the dilution factors of the HPIEC samples.
EXPERIMENT ISA.1005 — Ca(OH)$_2$, 28 °C, glove box

6.1 Concept

The experiment follows two purposes:

1. To study the effect of initial concentration of $\alpha$-ISA on the reaction rates of transformation at 28 °C.

2. To obtain reliable NPOC measurements (which was not the case in experiment ISA.1003).

3. To measure the influence of NaN$_3$, used as antimicrobial agent, and Fe(II) used as an O$_2$ scavenger on the reaction rates.

In contrast to experiment ISA.1003, which was carried out at similar boundary conditions, special care was taken to obtain more reliable NPOC results.

6.2 Experimental

The chemical transformation of $\alpha$-ISA was studied in the presence of 100 g dm$^{-3}$ Ca(OH)$_2$ as the solid phase using 50 µM or 100 µM as the initial concentrations of $\alpha$-ISA (or 0.3 and 0.6 mM C, respectively). The volumes of the liquid phases were of the order of 30 cm$^3$. All solutions and the reaction mixtures for these experiments were prepared in a glove box and kept in polysulfone tubes. All chemicals used were stored for several days in the glove box in order to remove traces of O$_2$ possibly sorbed to the solids. Fe(II) was added from an oxygen-free $10^{-2}$ M stock solution of Fe(II)SO$_4$·7H$_2$O in 1 mM H$_2$SO$_4$ to obtain a final concentration of $10^{-5}$ M Fe(II). The final concentration of NaN$_3$ was 1 mM. The reactions were started by adding defined amounts of an aqueous stock solution of $\alpha$-ISA-lactone to the mixtures of ACW-I and Ca(OH)$_2$.

After desired time periods the whole samples were filtered using a 0.2 µm Nylon membrane filter. The weights of the suspensions and the weights of the aliquot samples were monitored gravimetrically in order to keep control on mass losses owing to water evaporation. One part of the filtrates was directly diluted for the measurement of NPOC, and another part treated with OnGuard II H cartridges (cation exchangers in the protonated form) for the HPAEC, HPIEC and HPCEC analyses. All these steps
were carried out in the glove box. NPOC samples were kept at ambient temperature until measurement, whereas the samples for the chromatographic analyses that could not be analysed immediately were stored in polyethylene tubes at -20°C in a refrigerator.

### 6.3 Results obtained for reaction periods of ~50 days

The concentrations of α-ISA are plotted in Fig. 6.1 and the NPOC data in Fig. 6.2. The data are corrected for background concentrations of the analytes found in the blank systems containing Ca(OH)$_2$, but no α-ISA, and for the loss of water owing to evaporation occurring during sampling and during storage of the closed vessels. The latter correction factors varied between 1.00 and 1.01 and were thus negligible. The data for the reaction products are not shown here, however they amount to ~50% of the decrease of the concentration of α-ISA.

---

![Fig. 6.1:](image)

**Fig. 6.1:**
Transformation of α-ISA.
Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$
[ISA]$_{in}$: s. legend
26 ± 2°C
Polysulfone tubes
Multiple-batch
Glove box (N$_2$)

The experimental uncertainties were in general smaller than the symbol size.
6.4 Discussion

As already observed in experiment ISA.1003 an initial amount of 50 µM α-ISA is quantitatively transformed to reaction products within a period of 1 month. In contrast to the latter experiment, the present experiments show that only minor parts of α-ISA get lost from solution through sorption, as indicated by the constant concentrations of NPOC during the reaction. The present experiments also show that the rate of transformation is independent of the initial concentration of α-ISA, suggesting that a surface-mediated reaction mechanism is responsible for the transformation of α-ISA. The results further suggest that the transformation is not microbially mediated, however, this conclusion has to be treated with caution, because NaN₃ cannot prevent the growth of all types of microbes. It finally could be an indication that the reaction is not catalysed by traces of O₂, as the reaction proceeds at the same transformation rate in the presence of Fe(II) as in systems without Fe(II). This again is not conclusive in every respect, as it can be assumed that Fe(II) may quickly get oxidised in the presence of organic compounds at the high pH of the experiments.
7 EXPERIMENT ISA.1007 — Ca(OH)$_2$, 90 °C, glove box, test solid:liquid ratio

7.1 Concept

The experiment follows two purposes:

1. To measure kinetics as a function of solid to liquid ratio (abbreviated to S/L in the following) and of initial concentration of α-ISA.

2. To obtain large amounts of reaction products that could be used in radionuclide sorption experiments.

With respect to the second item, the experiments were planned as large batches, from which aliquot samples will be taken. The temperature was chosen to be 90 °C in order that reaction products would be formed in significant amounts within a reasonable time.

7.2 Experimental

The chemical transformation of α-ISA was studied in the presence of 50, 75 and 100 g dm$^{-3}$ Ca(OH)$_2$ as the solid phase using in each case 1.0 and 0.25 mM as the initial concentrations of α-ISA (or 6.0 and 1.5 mM C, respectively). The volumes of the liquid phases were of the order of 600 cm$^3$. All solutions and the reaction mixtures for these experiments were prepared in a glove box and kept in PTFE containers. All chemicals used were stored for several days in the glove box in order to remove traces of O$_2$ possibly sorbed to the solids. The closed PTFE containers were kept at 90 °C in an oven placed within the glove box. The reactions were started by adding a defined amounts of an aqueous stock solution of α-ISA-lactone to pre-heated mixtures of ACW-I and Ca(OH)$_2$.

After desired time periods aliquot samples of ~5 cm$^3$ were taken from the homogenised suspensions using a syringe. The weights of the suspensions and the weights of the aliquot samples were monitored gravimetrically in order to keep control on mass losses owing to water evaporation. The aliquot samples were allowed to cool down during 30 min. and then filtered using a 0.2 µm Nylon membrane filter. One part of the filtrates were directly diluted for the measurement of NPOC, and another part treated with OnGuard II H cartridges (cation exchangers in the protonated form) for the HPAEC,
HPIEC and HPCEC analyses. All these steps were carried out in the N\textsubscript{2}-atmosphere glove box. NPOC samples were kept at ambient temperature until measurement, whereas the samples for the chromatographic analyses that could not be analysed immediately, were stored in polyethylene tubes at –20°C in a refrigerator.

7.3 Results obtained for reaction periods of \textasciitilde200 days

The concentrations of $\alpha$-ISA, the overall carbon concentrations of possible reaction products and measured NPOC values are plotted in Figs. 7.1–7.3 for the experiments with an initial concentration of 1 mM (6 mM of carbon) and in Figs 7.4–7.6 for the experiments with an initial concentration of 0.25 mM (1.5 mM of carbon). The data are corrected for background concentrations of the analytes found in the blank systems containing Ca(OH)\textsubscript{2} but no $\alpha$-ISA and for the loss of water owing to evaporation occurring during sampling and during storage of the closed vessels. The latter correction factors vary between 1 and 1.04. In a few instances significant evaporation appears to have occurred in the aliquot samples used for the NPOC measurements as this is the only feasible explanation for the scatter in the NPOC data observed in isolated cases.

The measurements of the concentrations of reaction products are affected by rather large experimental uncertainties. This is due to the fact that higher concentrations of reaction products were expected. Some of these measurements were repeated using less diluted solutions in order to obtain more reliable results. It has also to be mentioned that the sum of reaction products is calculated using glycolate, formate and lactate concentrations only. The measurement of acetate was hampered in some measurements owing to an undulated baseline in the region of the acetate peak. After remediation of that problem it was found that, independent of the amount of Ca(OH)\textsubscript{2} and the initial concentration of $\alpha$-ISA, the concentration of acetate in the reaction mixtures was of similar order of magnitude as in the reference samples containing Ca(OH)\textsubscript{2}, but no $\alpha$-ISA. This shows that acetate can be neglected as a reaction product at high temperatures.
Fig. 7.1:
Influence of S/L on transformation of α-ISA.
Ca(OH)$_2$ (Fluka): s. legend
[ISA]$_{o}$: 1.0 mM (6.0 mM C)
90 ± 2°C
PTFE containers
Single-batch
Glove box (N$_2$)

Fig. 7.2:
Sum of reaction products of experiment shown in Fig. 7.1.
Ca(OH)$_2$ (Fluka): s. legend
[ISA]$_{o}$: 1.0 mM (6.0 mM C)
90 ± 2°C
PTFE containers
Single-batch
Glove box (N$_2$)
Fig. 7.3:
NPOC of experiment shown in Fig. 7.1.
Ca(OH)2 (Fluka): s. legend
[ISA]0: 1.0 mM (6.0 mM C)
90 ± 2°C
PTFE containers
Single-batch
Glove box (N2)

Fig. 7.4:
Influence of S/L on transformation of α-ISA.
Ca(OH)2 (Fluka): s. legend
[ISA]0: 0.25 mM (1.5 mM C)
90 ± 2°C
PTFE containers
Single-batch
Glove box (N2)
Fig. 7.5:
Sum of reaction products of experiment shown in Fig. 7.4.
\( \text{Ca(OH)}_2 \) (Fluka): s. legend
\([\text{ISA}]_0: 0.25 \text{ mM (1.5 mM C)}\)
90 ± 2°C
PTFE containers
Single-batch
Glove box (N\(_2\))

Fig. 7.6:
NPOC of experiment shown in Fig. 7.4.
\( \text{Ca(OH)}_2 \) (Fluka): s. legend
\([\text{ISA}]_0: 0.25 \text{ mM (1.5 mM C)}\)
90 ± 2°C
PTFE containers
Single-batch
Glove box (N\(_2\))
7.4 Discussion

For the discussion of the data observed in experiment ISA.1007 it is interesting to compare the data to those shown in Fig. 5.1 for experiment ISA.1003. Whereas in all the reactions in experiment ISA.1003 α-ISA was quantitatively transformed within ~50 d, the reactions in experiment ISA.1007 proceeded to a much lesser extent, and the data clearly suggest that the transformation reaction has reached some kind of equilibrium state. The only differences between the two experiments are the different methods of obtaining an oxygen-free atmosphere and the use of Ca(OH)$_2$ from different manufacturers. Although it appears unlikely, these differences seem to be the cause of the discrepant data.

The qualitative course of reaction at high temperature is very similar to the observations made at room temperature:

1. The disappearance of α-ISA from solution has mainly to be explained by a chemical transformation reaction. Owing to the relatively high level of NPOC values and the uncertainties associated, it is not possible to quantify a possible contribution by sorption processes.

2. The sum of identified reaction products is again of the order of 40 % of the concentration of α-ISA disappeared from solution. As already suggested by experiment ISA.1003 the product distribution is similar to that found at room temperature (not shown).

A further important question (with respect to a possible application of the outcome of this study in safety assessments) is whether the traces of O$_2$ in the glove box would be sufficient to explain the transformation of α-ISA observed in this experiment. Using a permeability coefficient of $2\cdot10^{-11}$ cm$^2$ sec$^{-1}$ Torr$^{-1}$ (22 °C) for PTFE, the geometry (surface, thickness) of a 1 dm$^3$ PTFE container and a maximum O$_2$ concentration of <5 ppm in the glove box, a diffusion rate of $\sim4\cdot10^{-10}$ mol O$_2$ per day at room temperature is obtained. The activation energy for diffusion of O$_2$ across PTFE materials was determined to be 10.5 kJ mol$^{-1}$ (DOBSON & TAYLOR, 1986). It was shown (GERRITSE, 1972) that such values may be used for extrapolation to high temperatures such as 90 °C. This gives an estimated rate of leakage of O$_2$ of $\sim10^{-9}$ mol O$_2$ per day into the experiments discussed here. This is negligible as compared to the observed transformation of $\sim2\cdot10^{-6}$ mol α-ISA per day (reached after 50 days of reaction). Direct reaction of traces of oxygen resulting in the transformation of α-ISA under glove box
conditions is therefore very unlikely as an explanation of the experimental observations.

8 EXPERIMENT ISA.1008 — Ca(OH)$_2$, 90 °C, glove box, test blocking of sites

8.1 Concept

Owing to the fact that $\alpha$-ISA was not quantitatively converted to transformation products in experiment ISA.1007, which was the original aim of that experiment, the production of substantial amounts of reaction products that might subsequently be used in radionuclide sorption studies, had to be abandoned. Instead a couple of the suspensions were used in the present experiment to further investigate possible reasons for the stopping of the reaction. Even if it cannot be expected that this question can be answered on the basis of a true reaction mechanism, it would be desirable to know if this effect is a property of the solid, of the solution composition, or of the composition of the atmosphere. For this reason, two of the suspensions from ISA.1007 were filtered, and fresh Ca(OH)$_2$ was added to the filtrates, and a fresh solution of $\alpha$-ISA in ACW-I was added to the filter residues. To a third suspension from ISA.1007 Ca(OH)$_2$ was added to obtain a S/L of ~150 g dm$^{-3}$. All experiments were performed at 90 °C.

8.2 Experimental

All steps are carried out under a controlled nitrogen atmosphere (O$_2$ < 5 ppm). Two existing suspensions (50 g dm$^{-3}$ and 100 g dm$^{-3}$ Ca(OH)$_2$) from experiment ISA.1007 initially containing 0.25 mM $\alpha$-ISA, in which the concentration of $\alpha$-ISA remained stable for several months, were filtered, and fresh amounts of Ca(OH)$_2$ were added to the filtrates. The filter residues were suspended in suitable volumes of an ACW-I solution containing 0.2 mM $\alpha$-ISA (1.2 mM C), in order to obtain again the previous S/L of 50 g dm$^{-3}$ and 100 g dm$^{-3}$.

To the 75 g dm$^{-3}$ Ca(OH)$_2$ suspension Ca(OH)$_2$ was added to obtain a S/L of 150 g dm$^{-3}$. 
The new suspensions were stored at a temperature of 90 °C in an oven placed in the glove box and subsequently sampled at regular time intervals. NPOC samples were kept at ambient temperature until measurement, whereas the samples for the chromatographic analyses that could not be analysed immediately were stored in polyethylene tubes at −20°C in a refrigerator.

8.3 Results and discussion

The concentration of α-ISA and the sum of possible reaction products are plotted in Figs. 8.1–8.6. Note that the data shown before the phase separation are those from ISA.1007. The data were corrected for background concentrations of the analytes found in the blank systems containing Ca(OH)$_2$, but no α-ISA and for the loss of water owing to evaporation occurring during sampling and during storage of the closed vessels. The latter correction factors vary between 1 and 1.03.

In all systems a restoration of the transformation reaction was observed upon addition of fresh Ca(OH)$_2$ to the filtrates or upon increasing the S/L. In contrast the addition of α-ISA to the filter residues induced much less transformation. Therefore, in this case, it is not entirely clear whether the amounts of transformation products can be regarded as being significant with respect to the background concentrations of these analytes.

**Fig. 8.1:**
*Behaviour of α-ISA after phase separation and re-equilibration of the suspensions from ISA.1007. Ca(OH)$_2$ (Fluka): 100 g dm$^{-3}$ [ISA]$i_0$: 0.25 mM (1.5 mM C) 90 ± 2°C PTFE containers Single-batch Glove box (N$_2$)*
**Fig. 8.2:**

Behaviour of reaction products after phase separation and re-equilibration of suspensions from ISA.1007:

- Ca(OH)$_2$ (Fluka): 100 g dm$^{-3}$
- [ISA]$_{in}$: 0.25 mM (1.5 mM C)
- 90 ± 2°C
- PTFE containers
- Single-batch
- Glove box ($N_2$)

**Fig. 8.3:**

Behaviour of α-ISA after phase separation and re-equilibration of suspensions from ISA.1007:

- Ca(OH)$_2$ (Fluka): 50 g dm$^{-3}$
- [ISA]$_{in}$: 0.25 mM (1.5 mM C)
- 90 ± 2°C
- PTFE containers
- Single-batch
- Glove box ($N_2$)
Fig. 8.4: 
Behaviour of reaction products after phase separation and re-equilibration of suspensions from ISA.1007:
$\text{Ca(OH)}_2$ (Fluka): 50 g dm$^{-3}$
$[\text{ISA}]_w$: 0.25 mM (1.5 mM C)
90 ± 2°C
PTFE containers
Single-batch
Glove box ($N_2$)

Fig. 8.5:
Behaviour of $\alpha$-ISA after phase separation and re-equilibration of suspensions from ISA.1007:
$\text{Ca(OH)}_2$: 150 g dm$^{-3}$ (after addition of fresh $\text{Ca(OH)}_2$)
$[\text{ISA}]_w$: 0.25 mM (1.5 mM C)
90 ± 2°C
PTFE containers
Single-batch
Glove box ($N_2$)
Although NPOC concentrations were not monitored in these experiments the increase in transformation products upon addition of fresh \( \text{Ca(OH)}_2 \) to the filtrates again demonstrates a chemical transformation of \( \alpha \)-ISA taking place and not simply sorption. The differences of the concentrations of \( \alpha \)-ISA and reaction products between the beginning and the stable phase of experiment ISA.1008 are similar to the differences observed in experiment ISA.1007. Similar amounts of \( \alpha \)-ISA were thus transformed in both experiments, and these amounts were again proportional to the amount of \( \text{Ca(OH)}_2 \) present in the suspensions.

It can be concluded that the stopping of the reaction is related to some property of the solid. As an example the alteration of the catalytic sites on the solid or consumption of possible impurities in \( \text{Ca(OH)}_2 \) could explain the observed behaviour of the system. In contrast the experiments demonstrate that the stopping of the reaction cannot be attributed to some property of the solution, such as its chemical composition. A feasible interpretation with the latter respect would have been the hypothesis that the active sites of the solid might have been blocked by the reaction products of the chemical transformation of \( \alpha \)-ISA. However these were — in contrast to all previous experiments — already present in solution from the start of experiment ISA.1008. A stopping of the reaction caused e.g. by sorption to the reaction sites by the reaction products of the chemical transformation themselves is consequently rather unlikely.
9 EXPERIMENT ISA.1009 — Ca(OH)$_2$, 28 °C, glove box, test O$_2$ limitation

9.1 Concept
The purpose of experiment ISA.1009 is to clarify, whether O$_2$ acts catalytically on the chemical transformation of α-ISA, or whether it acts as a reaction partner. Quantitative transformation of α-ISA would be possible in the presence of traces of O$_2$ in the first case, whereas in the second case the presence of stoichiometrically equivalent amounts of O$_2$ would be needed. There are indications from the earlier experiments that traces of O$_2$ may promote the transformation of α-ISA. However it would be desirable to clearly demonstrate, whether or not the stopping of the reaction is dependent on the amount of O$_2$ present.

9.2 Experimental
All steps were carried out under a controlled nitrogen atmosphere (O$_2$ < 5 ppm) in a glove box. Five suspensions of Ca(OH)$_2$ in ACW-I containing α-ISA were prepared. After verifying that the concentration of α-ISA remained approximately constant in these suspensions, defined amounts of O$_2$ were added in order to reach a stoichiometric excess or shortage of O$_2$ as compared to the α-ISA concentration. O$_2$ was added as air from an airtight syringe via a T-bore stopcock. It is an assumption that the PTFE vessels seal sufficiently in order for no significant losses of O$_2$ to occur. Experience from earlier experiments showed that the water loss from such vessels was not measurable in experiments carried out in the N$_2$-atmosphere glove box at room temperature, justifying this assumption. Liquid samples were also taken via the stopcock, in order to prevent the need to open the vessels. The suspensions were stored at ambient temperature and are subsequently sampled at regular time intervals. The weight of the PTFE containers was monitored during the course of the experiment in order to detect any loss of water by evaporation. It was found that the loss was less than the precision of the balance in the box (i.e. < 0.01 g within time spans of ~10 d). Samples were analysed for the concentrations of α-ISA, acetate, formate, glycolate, lactate.

Reaction conditions:

- Initial concentration of α-ISA: ~ 0.57 mM, amount of α-ISA: 3.4·10$^{-4}$ mol.
• Solid/Liquid ratio: 100 g dm\(^{-3}\).
• Amount of O\(_2\) added: 0, 10\(^6\) mol, 10\(^5\) mol, 10\(^4\) mol, 10\(^3\) mol (added as 0,
  0.12 cm\(^3\), 1.2 cm\(^3\), 12 cm\(^3\), and 120 cm\(^3\) of air at normal pressure).
• pH ~13.3 (ACW-I).
• ~28 °C.

Note that the stoichiometric equivalence of O\(_2\) and α-ISA — for the case that O\(_2\) is a reaction partner — is not exactly known. The highest amount of O\(_2\) is likely to be in excess compared to the amount of α-ISA, whereas all other amounts of O\(_2\) represent a stoichiometric shortage.

9.3 Results and discussion

The concentration of α-ISA and the sum of possible reaction products are plotted in Figs. 9.1 and 9.2. The data were corrected for background concentrations of the analytes found in the blank systems containing Ca(OH)\(_2\), but no α-ISA.

The initial phase of the reaction without O\(_2\) shows the typical behaviour already observed in experiments ISA.1001, ISA.1005 and ISA.1007. Upon addition of air a significant decrease in α-ISA concentration was observed in experiments with

![Fig. 9.1: Behaviour of α-ISA after addition of O\(_2\) (cf. the legend): Ca(OH)\(_2\) (Fluka): 100 g dm\(^{-3}\) [ISA]\(_{\text{in}}\): 0.57 mM (3.4 mM C) 28 ± 2°C PTFE containers Single-batch Glove box (N\(_2\))](image-url)
1.0 mmol of O₂ and a slight decrease in experiments with 0.1 mmol of O₂. In the other experiments the concentration of α-ISA remained identical with the reference system, to which no air was added, within the range of experimental uncertainty. Owing to the increased uncertainty of measurement for the reaction products as compared to the analysis of α-ISA, a significant increase in reaction products could only be observed for the experiment with 1.0 mmol of O₂. From these observations it may be concluded that O₂ acts as a reaction partner. If the role of O₂ was as a true catalyst, a significant turnover of α-ISA would have been also expected for the systems exhibiting a stoichiometric shortage of O₂ as compared to α-ISA.

Kinetic analysis of the data measured for the addition of 1 mmol of O₂ shows that most of the data fulfil first-order kinetic behaviour, whereas the last two data points deviate from such behaviour. Therefore it is not possible to determine whether the reaction slowed down because O₂ was running out, or because O₂ was not available for α-ISA within sufficient time, e.g. owing to slow diffusion of O₂ from the gas into the solution phase. For such a discrimination it would have been necessary to monitor the concentration of O₂ during the reaction. It is consequently not possible to unequivocally determine the stoichiometric ratio for the reaction between O₂ and α-ISA.
EXPERIMENT ISA.1004 — hardened cement paste, 28 °C, glove box

10.1 Overview

The chemical transformation of α-ISA in the presence of crushed hardened cement paste (HCP) as the solid phase was studied under nitrogen atmosphere in a glove box at the conditions given in Tab. 10.1. Owing to the strong sorption of α-ISA to HCP, significant parts of α-ISA are sorbed on HCP. Tab. 10.1 shows the distribution of α-ISA between HCP and ACW-I, as calculated from the sorption parameters given in VAN LOON et al. (1997). Experiments A-I1 and B-I2 are thus similar with respect to the amount of α-ISA sorbed, and experiments A-I1 and B-I3 with respect to the concentration of α-ISA in solution. The idea behind this parameter variation is to possibly draw conclusions on whether the chemical transformation of α-ISA is faster for molecules present in the solution or on the solid phase. Experiments A-I0 and B-I0 are blank systems containing no α-ISA, which are used as references for background concentrations of the analytes. Each six replicate samples per experimental type were prepared and harvested after different reaction times. The whole content of one sample was consumed for sampling. In order to be able to obtain a complete mass balance for the amount of carbon added to the experiments, the amount of α-ISA and the possible reaction products were measured both in the solution phase and on HCP after extraction with NaHCO₃.

Tab. 10.1: Experimental setup for investigating the chemical transformation of α-ISA in the presence of HCP.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>[α-ISA]₀ (mM)</th>
<th>HCP (g)</th>
<th>ACW-I (cm³)</th>
<th>(α-ISA)₀ eqᵃ (µmol)</th>
<th>(α-ISA)ₐorbᵇ (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-I0</td>
<td>0</td>
<td>0.05</td>
<td>5.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A-I1</td>
<td>1.66</td>
<td>0.05</td>
<td>5.0</td>
<td>5.0</td>
<td>3.3</td>
</tr>
<tr>
<td>B-I0</td>
<td>0</td>
<td>2.0</td>
<td>5.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B-I2</td>
<td>1.00</td>
<td>2.0</td>
<td>5.0</td>
<td>0.072</td>
<td>4.93</td>
</tr>
<tr>
<td>B-I3</td>
<td>27.2</td>
<td>2.0</td>
<td>5.0</td>
<td>5.0</td>
<td>131</td>
</tr>
</tbody>
</table>

ᵃ Amount of α-ISA present in the solution phase ᵇ Amount of α-ISA taken up by HCP
10.2 Experimental procedure

Ordinary Portland cement (CPA 55 HTS, Lafarge, France) was used for preparing cement pastes using a water:cement ratio of 0.7. These were hydrated for ~4 years in a humid N₂-atmosphere in a glove box at 28 °C and subsequently crushed and sieved to sizes between 0 and 70 µm.

All steps for preparation of the reaction suspensions and storage of these were carried out in a glove box under controlled N₂ atmosphere (CO₂, O₂ < 5 ppm). Filtration of the samples and the subsequent extraction was carried out under air atmosphere. All samples that could not be analysed immediately were stored in polyethylene tubes at –20 °C in a refrigerator.

Suspensions of HCP in ACW-I were prepared in 20 cm³ polypropylene scintillation vials. α-ISA was added as an aqueous solution of the lactone to these suspensions. The suspensions were shaken end-over-end at 28 °C for the desired reaction times. Control of weight of the vials showed that virtually no water was lost during storage of the samples. For harvesting of the samples the suspensions were filtered using a 20 cm³ vacuum filtration unit. Only ~2.5 cm³ of filtrate could be obtained from the suspensions with 400 g dm⁻³ of HCP. The different fractions (filtrate, wet filter residue, residue in the reaction vial, residue of filtrate in filtration apparatus) were weighed, in order to exactly quantify the fractions of liquid phase remaining in the solid and the water loss in the filtrate owing to evaporation of water during filtration. The filtrates were subsequently used for the various analyses, whereas the wet filter residues were quantitatively transferred to polysulfone centrifugation tubes in order to extract α-ISA (and possibly the reaction products) from HCP. 30 cm³ of 1 M NaHCO₃ were added to the concentrated suspensions (type B, cf. the sample names in Tab. 10.1) in order to extract the analytes from HCP, whereas 1 cm³ of 1 M NaHCO₃ plus 34 cm³ of H₂O were added in the case of the dilute suspensions (type A).

The extraction procedure using 1 M Na₂CO₃ is generally applied to extract concrete admixtures from hardened cement pastes (CONNOLLY et al., 1980). The presence of carbonate converts the various mineral phases containing Ca to CaCO₃, thus releasing organic acids, which are probably bound to the aluminate phases of HCP (VAN LOON et al., 1997; POELLMANN, 1992). The procedure was modified in using 1 M NaHCO₃ by GLAUS & VAN LOON (2004b) in order to extract gluconate from HCP, which sorbs even
more strongly than $\alpha$-ISA\textsuperscript{7}. The reason for using NaHCO$_3$ instead of Na$_2$CO$_3$ is to lower the pH as compared to extraction with Na$_2$CO$_3$, which decreases the tendency of gluconate to form surface and solution complexes. Various tests carried out in the frame of the present work (data not shown) have shown that an extraction time of 3 days is sufficient to quantitatively recover $\alpha$-ISA from HCP with 1 M NaHCO$_3$. During these tests it was also realised that substantial amounts of formate and acetate were mobilised from HCP. This — at a first glance quite unexpected — behaviour had important consequences for the concentration of possible reaction products measured in the reference experiments containing no $\alpha$-ISA\textsuperscript{8}.

For calculating the amount of analytes present in the solution phase of the samples containing $\alpha$-ISA, a series of corrections had to be undertaken in the following order:

1. Correction for evaporation of water during filtering of the samples.
2. Correction for analyte concentration in the corresponding blank experiment containing HCP, but no $\alpha$-ISA.

In order to calculate the amount of analytes taken up by HCP of the samples containing $\alpha$-ISA, the list of corrections applied is somewhat different:

1. Correction for the amount of analyte brought into the extraction via the fraction of ACW-I present in the wet suspensions. For this correction, the results of the analyses of the filtrates were used. In most of cases the amount originating from ACW-I was only between 1 and 10 % of the total amount of analyte present in the extraction solution and did not significantly increase the experimental uncertainty in the calculation of the amount of analyte bound to HCP.

2. Correction for analyte concentration in the corresponding blank experiment containing HCP, but no $\alpha$-ISA. In a few cases, negative values for the net concentrations of the reaction products were obtained after blank correction. However, the experimental uncertainty of the net values obtained was so large in these cases that it was reasonable to set these negative values to zero.

\textsuperscript{7}Gluconate is used in the cement industry as a superplasticiser and/or retarder in the production of cements with low water-to-cement ratios. Similarly to $\alpha$-ISA, gluconate is a strong complexant at high pH values.

\textsuperscript{8}In view of the fact that a variety of organic substances, e.g. grinding aids or substances that are "recycled by cementation" instead of being disposed of, are added during the production of cement clinker, the presence of low-molecular weight organic compounds is possible.
10.3 Results

In all systems investigated a decrease in solution concentration of $\alpha$-ISA and in the total amount of $\alpha$-ISA as a function of reaction time was observed within reaction times between 1 and 175 d (cf. Tab. 10.2). However, the relatively large error bars left the question open, whether this decrease was significant or not. If the chemical transformation of $\alpha$-ISA was a zero-order process — as could be expected from the initial experiments with Ca(OH)$_2$ as the solid phase — the longest experimental duration of 547 d would have been sufficient to unambiguously demonstrate a possible transformation of $\alpha$-ISA on the basis of the reactant’s concentration.

As shown by Tab. 10.2 the results of the measurements after 547 d are of the same order of magnitude as the results measured after a few days of contact. It has to be concluded from these results that it is not possible to demonstrate the chemical transformation based on the reactant’s concentration. It has to be noted that possible changes in the liquid volume owing to evaporation during storage in the box were negligible. The total weight of the suspensions after preparation and before sampling was monitored throughout.

**Tab. 10.2:** Analysis of $\alpha$-ISA in suspensions of HCP in ACW-I as a function of contact time.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Time (d)</th>
<th>$(\alpha$-ISA)$_{eq}$ (µmol)</th>
<th>$(\alpha$-ISA)$_{sorb}$ (µmol)</th>
<th>$(\alpha$-ISA)$<em>{eq}$ + $(\alpha$-ISA)$</em>{sorb}$ (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-I1-1</td>
<td>1</td>
<td>7.01 ± 0.25</td>
<td>1.67 ± 0.17</td>
<td>8.69 ± 0.31</td>
</tr>
<tr>
<td>A-I1-2</td>
<td>7</td>
<td>5.28 ± 0.19</td>
<td>2.27 ± 0.23</td>
<td>7.55 ± 0.30</td>
</tr>
<tr>
<td>A-I1-3</td>
<td>23</td>
<td>5.09 ± 0.18</td>
<td>2.51 ± 0.26</td>
<td>7.60 ± 0.32</td>
</tr>
<tr>
<td>A-I1-4</td>
<td>78</td>
<td>4.67 ± 0.17</td>
<td>3.13 ± 0.33</td>
<td>7.80 ± 0.37</td>
</tr>
<tr>
<td>A-I1-5</td>
<td>175</td>
<td>4.65 ± 0.17</td>
<td>2.59 ± 0.32</td>
<td>7.24 ± 0.36</td>
</tr>
<tr>
<td>A-I1-6</td>
<td>542</td>
<td>5.62 ± 0.38</td>
<td>2.64 ± 0.32</td>
<td>8.26 ± 0.49</td>
</tr>
<tr>
<td>B-I2-1</td>
<td>1</td>
<td>0.023 ± 0.007</td>
<td>4.62 ± 0.47</td>
<td>4.64 ± 0.47</td>
</tr>
<tr>
<td>B-I2-2</td>
<td>7</td>
<td>0.0086 ± 0.003</td>
<td>4.05 ± 0.42</td>
<td>4.06 ± 0.42</td>
</tr>
<tr>
<td>B-I2-3</td>
<td>23</td>
<td>0.0075 ± 0.003</td>
<td>3.79 ± 0.42</td>
<td>3.80 ± 0.42</td>
</tr>
<tr>
<td>B-I2-4</td>
<td>78</td>
<td>0.0079 ± 0.002</td>
<td>4.16 ± 0.47</td>
<td>4.17 ± 0.47</td>
</tr>
</tbody>
</table>
A graphical representation of the total amount of $\alpha$-ISA as a function of reaction time in relation to the amount of $\alpha$-ISA added to the systems is shown in Fig. 10.1. Note that the error bars in Fig. 10.1 are larger than the experimental uncertainties given in Tab. 10.2. The reason is that the latter uncertainties refer to the uncertainties of the analytical procedures only, whereas the error bars shown in Fig. 10.1 comprise also the uncertainties of the added amount of $\alpha$-ISA, which is assumed to be of the order of 5%.

![Graph showing total amount of $\alpha$-ISA as a function of reaction time]
The data shown in Fig. 10.1 suggest that $\alpha$-ISA was chemically transformed to a certain extent during the observation time of the experiments. However, the relatively large experimental uncertainties do not allow for unambiguous conclusions to be drawn. It can be seen also from this experiment that an ideal choice of conditions is absolutely crucial for an experiment to be significant. On one hand the experiments carried out with low amounts of $\alpha$-ISA are more sensitive to slight changes in analyte concentrations, on the other hand, the lower limit of the analytical window is restricted by the determination limits of the analytical procedures applied.

In order to draw conclusions on whether a transformation of $\alpha$-ISA is taking place during the experiments, it is important to consider the possible transformation products. However, as already mentioned in section 10.2, these compounds can also be found in the blank systems containing no $\alpha$-ISA. For this reason the results for all the experiments are represented without correction for blank values in Fig. 10.2 for the experiments carried out at a HCP:ACW-I ratio of 10 g dm$^{-3}$ and in Fig 10.3 for the experiments carried out at a HCP:ACW-I ratio of 400 g dm$^{-3}$. Figs. 10.4 and 10.5 show a comparison between the reaction systems and the corresponding blanks using representative HPIEC chromatograms. The plots also demonstrate the similarity of product distribution in experiments carried out in the presence of Ca(OH)$_2$ as the solid phase with the experiments, where HCP was used.

It is evident from Figs. 10.2 and 10.3 that the amount of reaction products found in the solution phase is larger in the systems containing $\alpha$-ISA than in the blanks containing no $\alpha$-ISA, suggesting that some transformation of $\alpha$-ISA is taking place. However, in the case of formate, glyolate and acetate, the background amounts found in the blanks are so large as compared to the amounts found in the solution phases, that one has to be careful in drawing conclusions on the reactivity of $\alpha$-ISA. Fortunately this situation is different in the case of lactate, which is an important transformation product in the experiments, where Ca(OH)$_2$ as the solid phase is used. The amount of lactate measured in the solution phase of the present experiment (ISA.1004) is significant when compared to the amount recovered from the solid. It is thus a clear indication that chemical transformation of $\alpha$-ISA is taking place even at ambient temperature in cementitious systems.

It can further be concluded from Figs. 10.2 and 10.3 that the amounts of reaction products recovered from HCP only depend on the amount of HCP added to the systems and not on the amount of $\alpha$-ISA added. This suggests that no sorption of the transformation products on HCP is taking place and that, in view of the relatively large
error bars, it is justified to set the blank-corrected amounts of reaction products recovered from HCP to zero. An open question in this context remains the fate of the transformation products. With increasing reaction time, less or even none of these products are recovered from HCP. It would be reasonable to assume that they are slowly mobilised from HCP during the equilibration with ACW-I. However equivalent amounts would have to be found in the solution phase, if this hypothesis was true. It is not clear, whether these compounds are susceptible to degradation (abiotical or microbial?) or whether they become immobile with respect to leaching by NaHCO$_3$ due to some unknown mechanism.

Tab. 10.3 finally shows the amounts of the possible transformation products found in the experiments carried out in the presence of $\alpha$-ISA after correction for the corresponding values found in the blank experiments containing no $\alpha$-ISA. The total amount of transformation products as a function of reaction time is inversely related to the decrease of $\alpha$-ISA. This comparison is only significant for experiments A-I1 and B-I2, where a significant decrease of $\alpha$-ISA can be demonstrated. This cannot be done in experiment B-I3, because of the large initial concentration of $\alpha$-ISA. The comparison shows for the measurements within the first 175 days that the total amount of transformation products cannot account for the decrease of $\alpha$-ISA. This is, however, of no surprise, because of the unexplained loss of these compounds that is also taking place in the blank systems. For the measurements after 542 days, an increase in the sum of reaction products is calculated. Most probably this is only an artefact, which arises from an underestimation of the uncertainties involved in the correction for the blank systems. The seeming increase in reaction products mainly arises from glycolate and formate, both compounds being present in large amounts in hardened cement paste from the beginning of the experiments.
Fig. 10.2: Amount of possible transformation products as a function of reaction time in experiments carried out at 10 g dm$^{-3}$ of HCP:ACW-I (Exp. A-I0 and A-I1). Left-hand column: Amount of transformation products in solution phase, right-hand column: Amount of transformation products originating from the solid. The symbols denote: ● Blank (A-I0), □ ($\alpha$-ISA)$_{0}$ = 8.3 µmol (A-I1).
Fig. 10.3: Amount of possible transformation products as a function of reaction time in experiments carried out at 400 g dm$^{-3}$ of HCP:ACW-I (Exp. B-I0, B-I2 and B-I3). Left-hand column: Amount of transformation products in solution phase, right-hand column: Amount of transformation products originating from the solid. The symbols denote: ● Blank (B-I0), □ (ISA)$_{in}$ = 5.4 µmol (B-I2), ▲ (ISA)$_{in}$ = 140 µmol (B-I3).
Fig. 10.4: HPIEC of filtrates from experiments with 10 g dm$^{-3}$ of HCP carried out at ambient temperature in the glove box. The legend indicates the sample name, reaction time and the dilution factor of the HPIEC sample.

Fig. 10.5: HPIEC of filtrates from experiments with 400 g dm$^{-3}$ of HCP as the solid phase carried out at ambient temperature in the glove box. The legend indicates the sample name, reaction time and the dilution factor of the HPIEC sample.
Tab. 10.3: Transformation products of α-ISA formed in suspensions of HCP in ACW-I at ambient temperature. All values are corrected for the amounts of the corresponding compounds contained in the blank systems A0 and B0.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Time (d)</th>
<th>(Formate)_{eq} (µmol C)</th>
<th>(Formate)_{lact} (µmol C)</th>
<th>(Glycolate)_{eq} (µmol C)</th>
<th>(Glycolate)_{lact} (µmol C)</th>
<th>(Lactate)_{eq} (µmol C)</th>
<th>(Lactate)_{lact} (µmol C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1-1</td>
<td>1</td>
<td>0.020 ± 0.01</td>
<td>0.020 ± 0.01</td>
<td>0.010 ± 0.01</td>
<td>0.010 ± 0.01</td>
<td>0.008 ± 0.01</td>
<td>0.008 ± 0.01</td>
</tr>
<tr>
<td>A-1-2</td>
<td>7</td>
<td>0.046 ± 0.03</td>
<td>0.046 ± 0.03</td>
<td>0.061 ± 0.04</td>
<td>0.061 ± 0.04</td>
<td>0.015 ± 0.02</td>
<td>0.015 ± 0.02</td>
</tr>
<tr>
<td>A-1-3</td>
<td>23</td>
<td>0.059 ± 0.01</td>
<td>0.059 ± 0.01</td>
<td>0.203 ± 0.02</td>
<td>0.203 ± 0.02</td>
<td>0.020 ± 0.03</td>
<td>0.020 ± 0.03</td>
</tr>
<tr>
<td>A-1-4</td>
<td>78</td>
<td>0.14 ± 0.0</td>
<td>0.14 ± 0.0</td>
<td>0.38 ± 0.0</td>
<td>0.38 ± 0.0</td>
<td>0.22 ± 0.0</td>
<td>0.22 ± 0.0</td>
</tr>
<tr>
<td>A-1-5</td>
<td>175</td>
<td>0.14 ± 0.0</td>
<td>0.14 ± 0.0</td>
<td>0.36 ± 0.0</td>
<td>0.1 ± 0.03</td>
<td>0.45 ± 0.0</td>
<td>0.50 ± 0.0</td>
</tr>
<tr>
<td>A-1-6</td>
<td>542</td>
<td>0.21 ± 0.0</td>
<td>0.21 ± 0.0</td>
<td>0.42 ± 0.1</td>
<td>0.42 ± 0.1</td>
<td>0.49 ± 0.1</td>
<td>0.49 ± 0.1</td>
</tr>
<tr>
<td>B-2-1</td>
<td>1</td>
<td>0.25 ± 0.1</td>
<td>0.25 ± 0.1</td>
<td>0.08 ± 0.1</td>
<td>0.08 ± 0.1</td>
<td>0.44 ± 0.2</td>
<td>0.44 ± 0.2</td>
</tr>
<tr>
<td>B-2-2</td>
<td>7</td>
<td>0.15 ± 0.0</td>
<td>0.15 ± 0.0</td>
<td>0.16 ± 0.0</td>
<td>0.16 ± 0.0</td>
<td>0.48 ± 0.0</td>
<td>0.48 ± 0.0</td>
</tr>
<tr>
<td>B-2-3</td>
<td>23</td>
<td>0.28 ± 0.0</td>
<td>0.28 ± 0.0</td>
<td>0.20 ± 0.0</td>
<td>0.20 ± 0.0</td>
<td>0.54 ± 0.0</td>
<td>0.54 ± 0.0</td>
</tr>
<tr>
<td>B-2-4</td>
<td>78</td>
<td>0.51 ± 0.0</td>
<td>-5.3 ± 1.8</td>
<td>-4.8 ± 1.8</td>
<td>0.29 ± 0.0</td>
<td>0.29 ± 0.0</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>B-2-5</td>
<td>175</td>
<td>0.56 ± 0.1</td>
<td>0.7 ± 1.4</td>
<td>1.3 ± 1.4</td>
<td>0.32 ± 0.0</td>
<td>0.32 ± 0.0</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>B-2-6</td>
<td>542</td>
<td>0.61 ± 0.1</td>
<td>3.9 ± 1.6</td>
<td>4.5 ± 1.6</td>
<td>0.35 ± 0.1</td>
<td>6.8 ± 2.9</td>
<td>7.15 ± 2.9</td>
</tr>
<tr>
<td>B-3-1</td>
<td>1</td>
<td>0.76 ± 0.0</td>
<td>0.76 ± 0.0</td>
<td>0.79 ± 0.7</td>
<td>0.79 ± 0.7</td>
<td>0.39 ± 0.2</td>
<td>0.39 ± 0.2</td>
</tr>
<tr>
<td>B-3-2</td>
<td>7</td>
<td>0.66 ± 0.0</td>
<td>0.66 ± 0.0</td>
<td>0.33 ± 0.1</td>
<td>0.33 ± 0.1</td>
<td>0.84 ± 0.2</td>
<td>0.84 ± 0.2</td>
</tr>
<tr>
<td>B-3-3</td>
<td>23</td>
<td>0.92 ± 0.1</td>
<td>0.92 ± 0.1</td>
<td>0.52 ± 0.2</td>
<td>0.52 ± 0.2</td>
<td>1.42 ± 0.2</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>B-3-4</td>
<td>78</td>
<td>1.1 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>0.55 ± 0.0</td>
<td>0.55 ± 0.0</td>
<td>2.9 ± 0.2</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>B-3-5</td>
<td>175</td>
<td>1.0 ± 0.1</td>
<td>0.3 ± 1.4</td>
<td>1.3 ± 1.4</td>
<td>0.52 ± 0.0</td>
<td>2.2 ± 0.1</td>
<td>2.2 ± 0.1</td>
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<tr>
<td>B-3-6</td>
<td>542</td>
<td>1.0 ± 0.1</td>
<td>11.4 ± 2.6</td>
<td>12.4 ± 2.6</td>
<td>0.67 ± 0.1</td>
<td>19.8 ± 3.8</td>
<td>20.51 ± 3.8</td>
</tr>
<tr>
<td>Sample name</td>
<td>Time (d)</td>
<td>((\text{Acetate})_{\text{aq}}) (µmol C)</td>
<td>((\text{Acetate})_{\text{act}}) (µmol C)</td>
<td>((\text{Acetate})_{pnh}) (µmol C)</td>
<td>Sum products (µmol C)</td>
<td>Decrease (\alpha)-ISA (^a) (µmol C)</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>---------</td>
<td>-------------------------------------</td>
<td>-------------------------------------</td>
<td>-------------------------------------</td>
<td>----------------------</td>
<td>-------------------------------------</td>
<td></td>
</tr>
<tr>
<td>A-II-1</td>
<td>1</td>
<td>0.020 ± 0.02</td>
<td>0</td>
<td>0.020 ± 0.02</td>
<td>0.058 ± 0.02</td>
<td>0.0 ± 0.0</td>
<td></td>
</tr>
<tr>
<td>A-II-2</td>
<td>7</td>
<td>0.051 ± 0.04</td>
<td>0</td>
<td>0.051 ± 0.04</td>
<td>0.16 ± 0.1</td>
<td>6.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>A-II-3</td>
<td>23</td>
<td>0.087 ± 0.02</td>
<td>0</td>
<td>0.087 ± 0.02</td>
<td>0.37 ± 0.0</td>
<td>6.5 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>A-II-4</td>
<td>78</td>
<td>0.11 ± 0.0</td>
<td>0</td>
<td>0.11 ± 0.0</td>
<td>0.86 ± 0.0</td>
<td>5.3 ± 0.4</td>
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<tr>
<td>A-II-5</td>
<td>175</td>
<td>0.15 ± 0.0</td>
<td>0.0 ± 0.04</td>
<td>0.18 ± 0.0</td>
<td>1.3 ± 0.1</td>
<td>8.7 ± 0.6</td>
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</tr>
<tr>
<td>A-II-6</td>
<td>542</td>
<td>0.09 ± 0.0</td>
<td>0</td>
<td>0.09 ± 0.0</td>
<td>1.2 ± 0.1</td>
<td>2.5 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>B-II-1</td>
<td>1</td>
<td>0.20 ± 0.7</td>
<td>0</td>
<td>0.20 ± 0.7</td>
<td>0.97 ± 0.6</td>
<td>0.0 ± 0.0</td>
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</tr>
<tr>
<td>B-II-2</td>
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<td>0.30 ± 0.0</td>
<td>0</td>
<td>0.30 ± 0.0</td>
<td>1.09 ± 0.1</td>
<td>3.5 ± 0.4</td>
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</tr>
<tr>
<td>B-II-3</td>
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<td>0.27 ± 0.0</td>
<td>0</td>
<td>0.27 ± 0.0</td>
<td>1.30 ± 0.1</td>
<td>5.0 ± 0.7</td>
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<tr>
<td>B-II-4</td>
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<td>0.42 ± 0.1</td>
<td>3.07 ± 1.6</td>
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<tr>
<td>B-II-5</td>
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<td>0.50 ± 0.1</td>
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<td>0.50 ± 0.1</td>
<td>3.2 ± 1.4</td>
<td>8.2 ± 1.3</td>
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<tr>
<td>B-II-6</td>
<td>542</td>
<td>0.69 ± 0.1</td>
<td>0</td>
<td>0.69 ± 0.1</td>
<td>13.6 ± 3.3</td>
<td>2.7 ± 0.4</td>
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<tr>
<td>B-III-1</td>
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<td>1.1 ± 0.3</td>
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<td>3.1 ± 0.8</td>
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<tr>
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<td>2.90 ± 0.3</td>
<td>54.7 ± 5.6</td>
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<tr>
<td>B-III-3</td>
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<td>0</td>
<td>1.1 ± 0.1</td>
<td>3.92 ± 0.3</td>
<td>37.9 ± 3.9</td>
<td></td>
</tr>
<tr>
<td>B-III-4</td>
<td>78</td>
<td>1.4 ± 0.1</td>
<td>0</td>
<td>1.4 ± 0.1</td>
<td>5.95 ± 0.2</td>
<td>-0.1 ± 0.0</td>
<td></td>
</tr>
<tr>
<td>B-III-5</td>
<td>175</td>
<td>1.3 ± 0.1</td>
<td>0</td>
<td>1.3 ± 0.1</td>
<td>5.3 ± 1.4</td>
<td>32.3 ± 3.4</td>
<td></td>
</tr>
<tr>
<td>B-III-6</td>
<td>542</td>
<td>1.0 ± 0.1</td>
<td>0</td>
<td>1.0 ± 0.1</td>
<td>36.5 ± 4.6</td>
<td>11.7 ± 1.3</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Decrease of total amount of \(\alpha\)-ISA between time \(t\) and \(t+1\) day.
11 EXPERIMENT ISA.1010 — compacted hardened cement paste or Ca(OH)$_2$,
28 °C, glove box

11.1 Concept

It is interesting to compare qualitatively the amount of $\alpha$-ISA transformed until the stopping of reaction occurred within the different systems investigated so far. Tab. 11.1 shows that both in Ca(OH)$_2$ and HCP systems similar amounts of $\alpha$-ISA were transformed until the stopping of the reactions, when normalising the amount of $\alpha$-ISA reacted for the amount of Ca(OH)$_2$ present (the fraction of Ca(OH)$_2$ in HCP is of the order of 15%). Note that the figures given in Tab. 11.1 have to be looked at as rough orders of magnitude only. The amount of $\alpha$-ISA reacted in the systems containing HCP are estimated based on the amounts of reaction products formed. As a working hypothesis it could be postulated that, on an absolute basis, 1 g of Ca(OH)$_2$ is able to convert 1µmol of $\alpha$-ISA to transformation products.

In view of the needs of a possible application of the results obtained in this study in performance assessment for the disposal of nuclear waste, it is an important question, whether the results obtained may be applicable to compacted systems, such as hydrated cement pastes. For this reason the transformation of $\alpha$-ISA was also studied.

Tab. 11.1: Comparison of $\alpha$-ISA in suspensions of HCP in ACW-I as a function of contact time (from various experiments).

<table>
<thead>
<tr>
<th>Solid</th>
<th>$[\alpha$-ISA]$_{in}$ (mM)</th>
<th>S/L ratio (g dm$^{-3}$)</th>
<th>T (°C)</th>
<th>$\alpha$-ISA reacted (%)</th>
<th>$\alpha$-ISA reacted (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>1.0</td>
<td>100</td>
<td>90</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>50</td>
<td>90</td>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>100</td>
<td>90</td>
<td>30</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>50</td>
<td>90</td>
<td>15</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>100</td>
<td>25</td>
<td>&gt;50</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>100</td>
<td>25</td>
<td>100</td>
<td>0.05</td>
</tr>
<tr>
<td>HCP</td>
<td>1.6</td>
<td>10</td>
<td>25</td>
<td>&lt;10 %</td>
<td>&lt;0.16</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>400</td>
<td>25</td>
<td>~20 %</td>
<td>~0.2</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>400</td>
<td>25</td>
<td>&lt;2 %</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>
in model systems containing Ca(OH)$_2$ and HCP at S/L in the range of 2000 to 3000 g dm$^{-3}$. Such degrees of compaction cannot be reasonably studied in batch sorption systems. A technique used for the study of diffusion processes in highly compacted clay systems was therefore applied for the present purpose in a modified version. The solids were compacted in a steel cell (cf. Fig. 11.1) to the desired dry bulk density and saturated with an ACW-I containing $\alpha$-ISA. After a certain reaction time the fluid was expelled and analysed for $\alpha$-ISA and possible products of chemical transformation.

Reaction times were chosen between 1 and 7 days, which is rather short when compared to other experiments in the present study. However a quantitative conversion of the total amount of $\alpha$-ISA to transformation products would be expected if the fast initial reaction rates and the S/L observed in ISA.1001 could be extrapolated to the conditions in the present experiment. Testing such a hypothesis was the focus here, rather than an investigation in detail of the kinetic behaviour of the degradation of $\alpha$-ISA in compacted solids.

![Fig. 11.1: Diffusion cell used for the study of chemical transformation in compacted Ca(OH)$_2$ or HCP saturated with $\alpha$-ISA containing ACW-I. The connections for the tubing's can be closed using bolts during the phase of reaction.](image)

### 11.2 Experimental

The preparation of compacted Ca(OH)$_2$ or HCP samples was carried out in air. Ca(OH)$_2$ or HCP was compressed directly in the steel rings of the diffusion cells to cylindrical dimensions of 2.56 cm in diameter and 1.04 cm in height. The target dry-bulk density of 1400 kg m$^{-3}$ was obtained under a load of $\sim$100 kN. After covering each side of the sample with a porous stainless steel filter disc (diameter: 2.56 cm, thickness: 1.55 mm, porosity $\sim$30 %, pore size 10 $\mu$m) and screwing together the
diffusion cells, the cells were transferred to the glove box and stood there for at least 72 h in order to achieve an O\textsubscript{2} free atmosphere in the void of the specimens.

All the following steps were carried out under a controlled nitrogen atmosphere (O\textsubscript{2} < 5 ppm). 3 – 7.5 cm\textsuperscript{3} of 5 mM \(\alpha\)-ISA (or a mixture of glycolate, formate, lactate and acetate for reference purposes) in ACW-I (prepared and stored in the glove box) were forced through the pore space of the sample using a HPLC pump at a flow of 0.2 to 0.5 cm\textsuperscript{3} min\textsuperscript{-1}. The amount of liquid in the pore space was determined according to the increase of the cell weight. Depending on the exact value of the dry-bulk density, the volume of the pore space was of the order of \(\sim\)1.7–2.0 cm\textsuperscript{3}. The S/L in the sample was thus of the order of 4000 to 4700 g dm\textsuperscript{-3}. From known dimension of the diffusion cell and the porous filter plates, a dead volume (pore space and channels) of 0.78 cm\textsuperscript{3} was also filled with solution. When assuming that the solutes in the dead volume were also available for contact with the sample through diffusive transport within the time of reaction, the effective S/L was thus 2800 to 3300 g dm\textsuperscript{-3}. After this saturating step the diffusion cell was closed using bolts and the cell was stored in the glove box for the desired reaction times of 0–7 days.

For the analysis of the amount of \(\alpha\)-ISA and possible reaction products the diffusion cell was removed from the glove box and flushed with 2 to 7.5 cm\textsuperscript{3} of ACW-I at a flow of 0.2 to 0.5 cm\textsuperscript{3} min\textsuperscript{-1} for the case of experiments with Ca(OH)\textsubscript{2}. In the case of experiments with HCP it was not possible to force ACW-I through the sample at a reasonable flow rate. The HCP samples were therefore removed from the diffusion cells, dried in the glove box at room temperature and ground to a fine powder using a mortar. The powder was then extracted using 1 M NaHCO\textsubscript{3} according to the procedures described in section 10.2. Note that \(\alpha\)-ISA would not have been measurable in the pore fluid owing to the very strong sorption at the high S/L used in these experiments.

Test experiments using Ca(OH)\textsubscript{2} spiked with known amounts of crystalline NaCl showed that it was possible to quantitatively recover the total amount of NaCl using the flushing volumes applied in the experiments. The full recovery also demonstrated that the compacted samples were homogeneously flushed with the liquid (data not shown).

11.3 Results and discussion

The raw data of all experiments carried out in the frame of experiment ISA.1010 are summarised in Tab. 11.2. Before going to details it can already be concluded from the
results that only minor parts of $\alpha$-ISA were converted to transformation products both in experiments with Ca(OH)$_2$ and HCP within the time of observation.

Tab. 11.2: Overview of the experimental conditions and on the analytical results of experiments carried out with compacted solids. Abbreviations: For (formate), Gly (glycolate), Lac (lactate), Ace (acetate).

<table>
<thead>
<tr>
<th></th>
<th>1010A-1</th>
<th>1010A-2</th>
<th>1010A-3</th>
<th>1010B-1</th>
<th>1010B-2</th>
<th>1010B-3</th>
<th>1010B-4</th>
<th>1010C-1</th>
<th>1010C-2</th>
<th>1010C-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(OH)$_2$ (Fluka)</td>
<td>7.993</td>
<td>7.917</td>
<td>7.926</td>
<td>7.423</td>
<td>7.421</td>
<td>7.442</td>
<td>7.456</td>
<td>7.567</td>
<td>7.492</td>
<td>7.467</td>
</tr>
<tr>
<td>V$_{sat}$ (cm$^3$)</td>
<td>2.00</td>
<td>3.00</td>
<td>3.00</td>
<td>7.50</td>
<td>7.50</td>
<td>7.50</td>
<td>7.50</td>
<td>7.50</td>
<td>3.00</td>
<td>7.50</td>
</tr>
<tr>
<td>V$_{emu}$ (cm$^3$)</td>
<td>1.70</td>
<td>1.69</td>
<td>1.62</td>
<td>1.83</td>
<td>1.91</td>
<td>1.91</td>
<td>1.67</td>
<td>2.09</td>
<td>2.12</td>
<td>1.95</td>
</tr>
<tr>
<td>S$_{sate}$ (g dm$^{-3}$)</td>
<td>4.66</td>
<td>4.66</td>
<td>4.60</td>
<td>4.03</td>
<td>4.66</td>
<td>3.99</td>
<td>4.47</td>
<td>3.63</td>
<td>3.52</td>
<td>3.83</td>
</tr>
<tr>
<td>S$_{tate}$ (g dm$^{-3}$)</td>
<td>3.22</td>
<td>3.20</td>
<td>3.35</td>
<td>2.85</td>
<td>2.76</td>
<td>2.79</td>
<td>2.90</td>
<td>2.63</td>
<td>2.54</td>
<td>2.69</td>
</tr>
<tr>
<td>Reaction time (d)</td>
<td>1.14</td>
<td>3.23</td>
<td>7.15</td>
<td>0.95</td>
<td>3.00</td>
<td>6.88</td>
<td>6.89</td>
<td>1.01</td>
<td>3.99</td>
<td>6.86</td>
</tr>
<tr>
<td>V$_{emu}$ (cm$^3$)</td>
<td>5.50</td>
<td>5.50</td>
<td>5.50</td>
<td>7.50</td>
<td>7.50</td>
<td>7.50</td>
<td>7.50</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

| $\alpha$-ISA$_{satu}$ (mol) | 8.73-10$^{-5}$ | 8.67-10$^{-5}$ | 8.31-10$^{-5}$ | 9.37-10$^{-5}$ | 9.79-10$^{-5}$ | 9.79-10$^{-5}$ | 8.54-10$^{-5}$ | 1.08-10$^{-5}$ | 1.10-10$^{-5}$ | 1.01-10$^{-5}$ |
| $\alpha$-ISA$_{base}$ (mol) | 3.99-10$^{-5}$ | 3.99-10$^{-5}$ | 3.98-10$^{-5}$ | 3.98-10$^{-5}$ | 3.97-10$^{-5}$ | 4.00-10$^{-5}$ | 4.25-10$^{-5}$ | 4.04-10$^{-5}$ | 4.00-10$^{-5}$ | 4.22-10$^{-5}$ |
| $\alpha$-ISA$_{act}$ (mol) | 1.27-10$^{-5}$ | 1.27-10$^{-5}$ | 1.23-10$^{-5}$ | 1.33-10$^{-5}$ | 1.38-10$^{-5}$ | 1.38-10$^{-5}$ | 1.28-10$^{-5}$ | 1.48-10$^{-5}$ | 1.50-10$^{-5}$ | 1.43-10$^{-5}$ |
| $\alpha$-ISA$_{ract}$ (mol) | 9.99-10$^{-5}$ | 9.99-10$^{-5}$ | 1.31-10$^{-5}$ | 1.98-10$^{-5}$ | 2.37-10$^{-5}$ | 2.45-10$^{-5}$ | 1.98-10$^{-5}$ | n.d. | 4.27-10$^{-5}$ | 4.02-10$^{-5}$ |
| Glycolate$_{emu}$ (mol) | 3.13-10$^{-7}$ | 3.51-10$^{-7}$ | 3.69-10$^{-7}$ | 4.44-10$^{-7}$ | 4.30-10$^{-7}$ | 4.01-10$^{-7}$ | 3.72-10$^{-7}$ | n.d. | 1.91-10$^{-5}$ | 1.99-10$^{-5}$ |
| Formate$_{emu}$ (mol) | 2.53-10$^{-7}$ | 4.22-10$^{-7}$ | 1.09-10$^{-6}$ | 2.12-10$^{-7}$ | 3.88-10$^{-7}$ | 5.17-10$^{-7}$ | 3.85-10$^{-7}$ | n.d. | 2.33-10$^{-6}$ | 2.49-10$^{-6}$ |
| Lactate$_{emu}$ (mol) | 1.31-10$^{-7}$ | 3.21-10$^{-7}$ | 5.46-10$^{-7}$ | 4.31-10$^{-7}$ | 3.14-10$^{-7}$ | 8.21-10$^{-7}$ | 7.52-10$^{-7}$ | n.d. | 5.38-10$^{-7}$ | 4.65-10$^{-7}$ |
| Acetate$_{emu}$ (mol) | 1.64-10$^{-10}$ | 1.31-10$^{-7}$ | 1.65-10$^{-7}$ | 1.14-10$^{-7}$ | 1.48-10$^{-7}$ | 1.52-10$^{-7}$ | 1.26-10$^{-7}$ | n.d. | 9.87-10$^{-7}$ | 1.19-10$^{-6}$ |

*Volume applied for saturation of the diffusion cells. Not included in the figures tabulated is the volume used to fill all the voids of the cell, i.e. V$_{emu}$ and V$_{base}$.

*Calculated from the increase in weight of the cell, corrected for the cell dead volume (s. footnote a).

*Considering V$_{emu}$ only for calculation.

*Considering V$_{emu}$ plus V$_{base}$ for calculation.

*Volume applied for flushing the cell with ACW-I.

*Amount of $\alpha$-ISA in pore volume of the solid, calculated based on solution concentration and pore volume (cf. eqn. (10.1)).

*Amount of $\alpha$-ISA in dead volume of the diffusion cell, calculated based on solution concentration and dead volume (cf. eqn. (10.1)).

*Sum of (\alpha-ISA)$_{satu}$ plus (\alpha-ISA)$_{base}$ (cf. eqn. (10.1)).

*The index ract stands for the amount recovered: upon flushing with ACW-I in the case of Ca(OH)$_2$, and by extraction in the case of HCP.
This is — among more important conclusions — an indication that the assumption of an oxygen-free atmosphere was valid. For a reliable calculation of the amount of α-ISA reacted, it is necessary to know the amount of α-ISA brought into the cell during the flushing with the solution of α-ISA in ACW-I. As already suggested by the previous experiments in more diluted suspensions, a slight tendency of α-ISA to sorb onto Ca(OH)$_2$ was observed. At the high S/L used in the present experiments, it can be expected that the amount of α-ISA sorbed to Ca(OH)$_2$ is even higher than in diluted suspensions. However, the exact amount of α-ISA sorbed is not experimentally accessible in the case of Ca(OH)$_2$. The case is different for HCP, where it can be reliably assumed that α-ISA is almost quantitatively sorbed to HCP (Van Loon et al., 1997).

Useful evidences for a rough estimate for the amount of α-ISA sorbed to Ca(OH)$_2$ can be found, however, from a comparison of the results of experiments ISA.1010A and ISA.1010B (cf. Tab. 11.2). Experiment ISA.1010B is actually a repetition of ISA.1010A with the modification that S/L was chosen slightly lower in order to allow for higher flow rates to be set and thereby increasing the flushing rate. In both experiments, the amount of α-ISA recovered during the flushing with ACW-I is larger than simply calculated on the basis of (α-ISA)$_{sol}$, the amount of α-ISA present in the pore fluid and the dead volume of the diffusion cell (cf. the figures given for (α-ISA)$_{sol}$):

\[
(\alpha\text{-ISA})_{sol} = [\alpha\text{-ISA}]_{in} \cdot \frac{(V_{por} + V_{dead})}{1000}
\]  

(11.1)

where:

- [α-ISA]$_{in}$: Concentration of α-ISA in the solution used to saturate the diffusion cell (M)
- $V_{por}$: Volume of the pore space of the compacted solid (cm$^3$)
- $V_{dead}$: Dead volume of the diffusion cell (cm$^3$), comprising the porosity of the porous filter plates plus the volume of the internal channels. $V_{dead}$ was measured to be 0.78 cm$^3$.

However, the results further suggest that increasing amounts of α-ISA are recovered from the diffusion cells with increasing incubation time. This observation makes no sense at a first glance. A possible explanation for this seeming inconsistency is probably found in an uneven distribution of α-ISA across the sample and in a slightly incomplete recovery. Note that minor deviations from a 100% recovery of α-ISA are not in contradiction with the complete recovery of chloride, because the latter does not
sorb on Ca(OH)$_2$. $\alpha$-ISA sorbed to the solid will be enriched in the part near to the inlet of the diffusion cell. It would make sense that the recovery of a cell with $\alpha$-ISA enriched near the inlet would be lower than in a cell with an even distribution of $\alpha$-ISA, if the recovery is not complete. This would be a qualitative explanation for the generally lower recovery in experiment ISA.1010A as compared to experiment ISA.1010B, because the solids in the latter experiment were contacted with more $\alpha$-ISA solution in ACW-I and subsequently flushed with more ACW-I after the reaction time. Also the increasing recoveries with increasing reaction time can be understood in the light of this hypothesis. The longer standing times lead to a gradual re-equilibration of the uneven distribution of $\alpha$-ISA owing to diffusive processes. Consequently the recovery of a cell with longer reaction time will be better than for a cell with short reaction time.

Tab. 11.3 shows an attempt to quantify the effects of sorption to Ca(OH)$_2$ on the recovery of $\alpha$-ISA. It is assumed that the amount of $\alpha$-ISA sorbed to Ca(OH)$_2$ is linearly dependent on the difference between the contact volume, $V_{\text{con}}$ (cm$^3$), the total volume of $\alpha$-ISA solution in ACW-I brought into contact with the solid (measured at the midpoint of the solid specimen), and $V_{\text{por}}$:

$$V_{\text{con}} = V_{\text{sat}} + (V_{\text{por}} + V_{\text{dead}}) \cdot 0.5$$  \hspace{1cm} (11.2)

Whereas only smaller parts of $\alpha$-ISA present in $V_{\text{con}}$ will sorb on Ca(OH)$_2$, it was assumed that the total amount of $\alpha$-ISA present in $V_{\text{con}}$ gets sorbed on HCP. The estimates for the amounts of $\alpha$-ISA sorbed to the solids are given in Tab. 11.3. Also given in Tab. 11.3 are estimates for the recovery during the flushing. As already mentioned it is assumed that the recoveries depend on the flushing volume and on the reaction time (i.e. on the time for re-equilibration of possible gradients owing to diffusive processes). The combined effect of these cannot be quantitatively assessed, and thus, the figures given in Tab. 11.3 have to be regarded as "reasonable guesses". However

---

9 As an example one may compare distribution coefficients, $R_d$ (the amount of a species sorbed per gram of solid divided by the solution concentration of that species): $R_d$ for sorption of $\alpha$-ISA on Ca(OH)$_2$ in experiment ISA.1010B is of the order of $3 \cdot 10^{-4}$ dm$^3$ g$^{-1}$. If it is assumed that 5% of the [\$\alpha$-ISA]$_S$ get sorbed in experiments with S/L of 100 g dm$^{-3}$ (cf. e.g. Fig. 6.2), an $R_d$ of $5 \cdot 10^{-4}$ dm$^3$ g$^{-1}$ results. Simple sorption models, such as a Langmuir isotherm, predict that $R_d$ is independent of S/L, as long as the maximum sorption capacity of the solid for the species under consideration is not reached, an assumption which certainly applies for the present conditions.
the uncertainties brought into the mass balance of α-ISA by these guesses are of rather secondary importance on the whole.

Tab. 11.3: Mass balance for α-ISA and reaction products in the experiments with compacted solids under the assumptions made for sorption of α-ISA and incomplete recovery (cf. text).

<table>
<thead>
<tr>
<th></th>
<th>1010A-1</th>
<th>1010A-2</th>
<th>1010A-3</th>
<th>1010B-1</th>
<th>1010B-2</th>
<th>1010B-3</th>
<th>1010B-4</th>
<th>1010C-1</th>
<th>1010C-2</th>
<th>1010C-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{sol}}$ (cm$^3$)</td>
<td>3.24</td>
<td>4.23</td>
<td>4.20</td>
<td>8.80</td>
<td>8.84</td>
<td>8.84</td>
<td>8.75</td>
<td>n.d.</td>
<td>8.95</td>
<td>8.88</td>
</tr>
<tr>
<td>(α-ISA)$_{\text{mes}}$ (mol) $^a$</td>
<td>5.00·10$^7$</td>
<td>2.00·10$^5$</td>
<td>2.00·10$^5$</td>
<td>1.25·10$^5$</td>
<td>1.25·10$^5$</td>
<td>1.25·10$^5$</td>
<td>1.25·10$^5$</td>
<td>n.d.</td>
<td>4.62·10$^5$</td>
<td>4.58·10$^5$</td>
</tr>
<tr>
<td>(α-ISA)$_{\text{sat}}$ (mol) $^b$</td>
<td>1.32·10$^5$</td>
<td>1.47·10$^5$</td>
<td>1.63·10$^5$</td>
<td>2.56·10$^5$</td>
<td>2.63·10$^5$</td>
<td>2.63·10$^5$</td>
<td>2.53·10$^5$</td>
<td>n.d.</td>
<td>4.62·10$^5$</td>
<td>4.58·10$^5$</td>
</tr>
<tr>
<td>$f_{\text{rec}}$ (%) $^c$</td>
<td>80</td>
<td>85</td>
<td>98</td>
<td>80</td>
<td>85</td>
<td>98</td>
<td>98</td>
<td>n.d.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(α-ISA)$_{\text{g}}$ (mol C) $^d$</td>
<td>4.45·10$^6$</td>
<td>7.18·10$^5$</td>
<td>5.25·10$^5$</td>
<td>6.29·10$^5$</td>
<td>-1.01·10$^3$</td>
<td>7.93·10$^5$</td>
<td>3.05·10$^5$</td>
<td>n.d.</td>
<td>2.11·10$^5$</td>
<td>3.36·10$^5$</td>
</tr>
<tr>
<td>$\Sigma$(Prod)$_{\text{g}}$ (mol C) $^e$</td>
<td>1.60·10$^6$</td>
<td>2.35·10$^6$</td>
<td>3.80·10$^6$</td>
<td>2.40·10$^6$</td>
<td>2.52·10$^6$</td>
<td>3.78·10$^5$</td>
<td>3.27·10$^6$</td>
<td>n.d.</td>
<td>9.74·10$^6$</td>
<td>1.02·10$^5$</td>
</tr>
<tr>
<td>$\Sigma$(Prod)$_{\text{b}}$ (mol C) $^f$</td>
<td>4.00·10$^6$</td>
<td>5.88·10$^6$</td>
<td>9.50·10$^6$</td>
<td>6.00·10$^6$</td>
<td>6.29·10$^6$</td>
<td>9.45·10$^6$</td>
<td>8.17·10$^6$</td>
<td>n.d.</td>
<td>2.43·10$^5$</td>
<td>2.56·10$^5$</td>
</tr>
</tbody>
</table>

$^a$ Estimated from proportionality in the case of Ca(OH)$_2$; calculated as the amount of α-ISA contained in $V_{\text{sol}}$ in the case of HCP.

$^b$ Sum of (α-ISA)$_{\text{mes}}$ plus (α-ISA)$_{\text{sat}}$ (cf. eqn. (10.3)).

$^c$ Recovery of α-ISA after flushing the cell with ACW-I.

$^d$ Calculated according to eqn. (10.4).

$^e$ Sum of identified reaction products (cf. Tab. 10.2).

$^f$ Calculated under the assumption that the reaction products identified amount to 40 % of the total amount of reaction products.
The mass balance of $\alpha$-ISA is composed from the total amount of $\alpha$-ISA present in the diffusion cell, $(\alpha$-ISA)$_{tot}$ (mol),

$$(\alpha$-ISA)$_{tot} = (\alpha$-ISA)$_{sol} + (\alpha$-ISA)$_{sorb}$$  \hspace{1cm} (11.3)

and the amount of $\alpha$-ISA recovered upon flushing with ACW-I, $(\alpha$-ISA)$_{rec}$. The amount of $\alpha$-ISA reacted to transformation products, $(\alpha$-ISA)$_{rg}$ can be assessed either by the difference between $(\alpha$-ISA)$_{tot}$ and $(\alpha$-ISA)$_{rec}$,

$$(\alpha$-ISA)$_{rg} = (\alpha$-ISA)$_{tot} - (\alpha$-ISA)$_{rec} \cdot 100$$  \hspace{1cm} (11.4)

or by multiplying the sum of identified reaction products by a factor 2.5 under the assumption that the latter amount to $\sim$40 % of the amount of total reaction products. It has been demonstrated in accompanying control experiments that the reaction products are fully recovered from compacted Ca(OH)$_2$, after saturation of diffusion cells with a solution of defined concentrations of the reaction products in ACW-I (data not shown). In these control experiments it turned out that glycolate shows a similar tendency to sorb onto Ca(OH)$_2$ as observed for $\alpha$-ISA, whereas the other reaction products did not show any sorption.

It is obvious that an exact determination of $(\alpha$-ISA)$_{rg}$ is largely dependent on the assumptions made for sorption to Ca(OH)$_2$ and incomplete recovery. The overall uncertainty of $(\alpha$-ISA)$_{rg}$ is large, because it is formed as the difference between two similar figures. In any case $(\alpha$-ISA)$_{rg}$ calculated based on a mass balance for $\alpha$-ISA is of a similar order of magnitude as $(\alpha$-ISA)$_{rg}$ calculated based on the sum of reaction products. In this respect the assumptions made seem to be rather reasonable. For a direct comparison of the experiments, however, and for a comparison of the amount of $(\alpha$-ISA)$_{rg}$, it is more reliable to use the amount of reaction products as a measure for the turnover of $\alpha$-ISA. Although these values are also subject to uncertainty, the uncertainties involved are of systematic type, i.e. their relative value is the same for all experiments. In contrast, the uncertainties involved in the calculation of $(\alpha$-ISA)$_{rg}$ using eqn. (11.4) are rather of statistical type and may not be the same for all experiments. Further the amount of reaction products is not dependent on the assumptions made for sorption and incomplete recovery.

A graphical representation of the mass balances obtained is given by Figs. 11.2a, 11.2b and 11.2c. It can be concluded from these data that only minor parts of $\alpha$-ISA are
converted to transformation products. A slight tendency of increasing turnover of $\alpha$-ISA with increasing incubation time may be notified in the data.

Fig. 11.2a:
Mass balance for $\alpha$-ISA and reaction products in experiment ISA.1010A. The amount of $\alpha$-ISA reacted is based on estimates for $\alpha$-ISA sorbed to Ca(OH)$_2$ and for incomplete recovery (cf. Tab. 11.3) and is probably less reliable for assessing the turnover rate of $\alpha$-ISA as compared to the sum of reaction products. Solid = Ca(OH)$_2$ at an effective S/L of ~3300 g dm$^{-3}$

Fig. 11.2b:
Mass balance for $a$-ISA and reaction products in experiment ISA.1010B. The amount of $a$-ISA reacted is based on estimates for $a$-ISA sorbed to Ca(OH)$_2$ and for incomplete recovery (cf. Tab. 11.3) and is probably less reliable for assessing the turnover rate of $a$-ISA as compared to the sum of reaction products. Solid = Ca(OH)$_2$ at an effective S/L of ~2800 g dm$^{-3}$
Fig. 11.2c:

Mass balance for $\alpha$-ISA and reaction products in experiment ISA.1010C. The amount of $\alpha$-ISA reacted is based on estimates for $\alpha$-ISA sorbed to Ca(OH)$_2$ and for incomplete recovery (cf. Tab. 11.3) and is probably less reliable for assessing the turnover rate of $\alpha$-ISA as compared to the sum of reaction products. Solid = HCP at an effective S/L of $\sim$2600 g dm$^{-3}$.

When comparing the amounts of reaction products formed with the initially expressed working hypothesis of 1 $\mu$mol $\alpha$-ISA being converted per gram of Ca(OH)$_2$ present, the values calculated are within the correct order of magnitude. Note that they are higher for HCP, if the values are normalised to the percentage content of Ca(OH)$_2$ in HCP. However there are two uncertainties in this assumption: (i) It is not clear, whether the oxidising activity has to be traced back to Ca(OH)$_2$ or to the integral solid, and (ii) the sum of reaction products was not corrected for possible background values for HCP. Concerning the second point, one has to assume that the values given in Tab. 11.3 rather tend to overestimate the true values.
12 EXPERIMENT ISA.1011 — Ca(OH)$_2$, 28 / 90 °C, glove box

12.1 Concept

This is virtually a repetition of experiment ISA.1005 with the aim to test the repeatability, especially in view of the extent of transformation of $\alpha$-ISA with time. Further two batches of Ca(OH)$_2$ from different suppliers were tested.

12.2 Experimental

5 test single-batch systems were set up according to Tab. 12.1 in PTFE containers. All other steps were carried out according to the procedures described in ISA.1005 and ISA.1007 (especially concerning the steps necessary to carry out experiments at high temperature under exclusion of air: "Acclimatisation" of chemicals in the glove box and using an oven within the glove box).

Tab. 12.1: Overview of the experimental conditions applied in experiment ISA.1011. All experiments were carried out as single-batches in PTFE containers.

<table>
<thead>
<tr>
<th>Solid</th>
<th>ISA.1011A</th>
<th>ISA.1011B</th>
<th>ISA.1011C</th>
<th>ISA.1011D</th>
<th>ISA.1011E</th>
</tr>
</thead>
<tbody>
<tr>
<td>~Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>Fluka</td>
<td>Fluka</td>
<td>Merck</td>
<td>Fluka</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\alpha$-ISA]$_{in}$ (mM)</td>
<td>0.05</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>$[\alpha$-ISA]$_{in}$ (mM C)</td>
<td>0.30</td>
<td>0.60</td>
<td>0.30</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>T (°C)</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Box $^b$</td>
<td>Box $^b$</td>
<td>Box $^b$</td>
<td>Box (oven) $^b$</td>
<td>Box (oven) $^b$</td>
</tr>
</tbody>
</table>

$^a$ All experiments were carried out at S/L of 100 g dm$^{-3}$.

$^b$ N$_2$-atmosphere glove box

12.3 Results

The results are shown in Figs 12.1 – 12.5. The abscissa of these plots are broken between 15 and 75 d for better representation of the data. No measurements were made during that interval. Figs 12.1 – 12.5 confirm previous observations made in experiments ISA.1005, 1007 and 1008:

- The transformation reaction proceeds only to a limited extent. At the conditions applied $\alpha$-ISA seems to be in excess compared to its "reaction partner". This
can be seen when comparing experiments with different initial concentrations of \( \alpha \)-ISA. The \( \alpha \)-ISA concentration converted to transformation products is between 0.04 and 0.05 mM in all experiments regardless of the initial concentration of \( \alpha \)-ISA. Also the sum of reaction products measured is similar for all experiments.

**Fig. 12.1: ISA.1011A**

Concentration of \( \alpha \)-ISA and reaction products as a function of time.

\( \text{Ca(OH)}_2 \) (Fluka): 100 g dm\(^{-3}\)

\([\text{ISA}]_0\): 0.05 mM (0.3 mM C)

28 ± 2°C

Vessel type: PTFE

Single-batch

Inert-gas box

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**Fig. 12.2: ISA.1011B**

Concentration of \( \alpha \)-ISA and reaction products as a function of time.

\( \text{Ca(OH)}_2 \) (Fluka): 100 g dm\(^{-3}\)

\([\text{ISA}]_0\): 0.10 mM (0.6 mM C)

28 ± 2°C

Vessel type: PTFE

Single-batch

Inert-gas box
Fig. 12.3: ISA.1011C
Concentration of α-ISA and reaction products as a function of time.
Ca(OH)$_2$ (Merck): 100 g dm$^{-3}$
[ISA]$_0$: 0.10 mM (0.6 mM C)
28 ± 2°C
Vessel type: PTFE
Single-batch
Inert-gas box

Fig. 12.4: ISA.1011D
Concentration of α-ISA and reaction products as a function of time.
Ca(OH)$_2$ (Fluka): 100 g dm$^{-3}$
[ISA]$_0$: 0.10 mM (0.6 mM C)
90 ± 2°C
Vessel type: PTFE
Single-batch
Inert-gas box
There are no significant qualitative differences between the reaction carried out at room temperature and 90 °C, with the exception of a faster initial reaction rate at 90 °C. This observation is a main reason to exclude microbial processes as a reason for the chemical transformation of α-ISA. Also, there would seem little reason why microbial action should stop after relatively short period of time.

The stopping of the reaction gives similar concentrations at both temperatures. Again this observation is in contrast to the results obtained in ISA.1003, where much larger initial concentrations of α-ISA were quantitatively converted to reaction products.

No significant difference was found between using Ca(OH)$_2$ from Merck or Fluka. Consequently the use of different sources for Ca(OH)$_2$ cannot be the reason for the different extent of transformation reaction observed.
13 SUMMARY AND OVERALL CONCLUSIONS

Taking together the results of all experiments a fairly consistent picture is obtained leading to the following main conclusions:

1. $\alpha$-ISA is only converted quantitatively to reaction products if $O_2$ (or maybe another oxidising agent) is present in stochiometrically equivalent amounts (cf. ISA.1009). The identified reaction products, glycolate, formate, lactate and acetate have less complexing strength compared to $\alpha$-ISA.

2. In the absence of $O_2$, the transformation reaction proceeds, independently of the S/L tested, only to a limited extent (ISA.1001, ISA.1005, ISA.1007, ISA.1008, ISA.1011). As a working hypothesis (or a rule-of-thumb), one may estimate that 1 $\mu$mol of $\alpha$-ISA is converted to transformation products per gram of solid, be this Ca(OH)$_2$ or HCP (rough average from all the experiments mentioned). If the amount of $\alpha$-ISA present exceeds this limit, $\alpha$-ISA was shown to be stable for observation times of several months (ISA.1004, ISA.1007, ISA.1008).

3. The concentration of reaction products and measurements of NPOC in the solution phase clearly demonstrate that, even under anoxic conditions, a chemical transformation is actually the main reason for the loss of $\alpha$-ISA from solution in the case of experiments carried out with Ca(OH)$_2$ (best accuracy obtained in ISA.1005). Sorption of $\alpha$-ISA to Ca(OH)$_2$ may, however, contribute in a minor way to the loss of $\alpha$-ISA from the solution phase.

4. If $O_2$ is involved in the chemical transformation of $\alpha$-ISA, it reacts stoichiometrically with $\alpha$-ISA. A catalytic involvement of $O_2$ can be excluded.

5. Microbial transformation reactions are not of importance under the conditions of the present experiments. This is especially underlined by direct comparison of experiments carried out at room temperature and at 90 °C in experiment ISA.1011.

These conclusions are in agreement with the observations of GREENFIELD et al. (1995) and HURDUS & PILKINGTON (2000), who found that the slight decrease of $\alpha$-ISA concentration observed was larger under aerobic than under anaerobic conditions. Those experiments were carried out in homogeneous, Ca(OH)$_2$ saturated solutions. The work described in this report shows that the presence of a solid phase, such as Ca(OH)$_2$, leads to a faster turnover of the chemical transformation of $\alpha$-ISA compared to homogeneous systems.
In view of the use of the results in the safety assessment of a repository for radioactive waste one may conclude that the observed chemical transformation of $\alpha$-ISA cannot be used as a justification to postulate $\alpha$-ISA concentrations being decreased to insignificant amounts under chemically-reducing repository conditions. Further, it is not justifiable to apply the above-mentioned rule-of-thumb to repository conditions, because the actual reason for transformation of $\alpha$-ISA under anoxic conditions could not be unequivocally identified in the frame of this work. Quantitative turnover of $\alpha$-ISA was observed only in the presence of $O_2$. Such conditions do not apply for the conditions in an underground cementitious repository. Although it is not possible to demonstrate that $\alpha$-ISA will be stable over repository time scales, one may note that such an assumption is conservative in the sense of performance assessment, because the radionuclides complexed by $\alpha$-ISA will be more mobile than in a situation without $\alpha$-ISA. The complexation by $\alpha$-ISA may lead to an enhanced solution concentration of many radionuclides by increasing their solubility limits and decreasing their sorption.

The identification of the reaction partners under anaerobic conditions and of possible reaction pathways leading to the reaction products observed has not been possible in this work. A formal reaction of $\alpha$-ISA with an oxidising agent ("Ox", equivalent to $O_2$) like

$$C_6H_{12}O_6 + "Ox" \rightarrow CH_2OHCOOH + HCOOH + CH_3CHOHCOOH$$

(13.1)

could be used to roughly characterise the processes observed and for rough mass balance considerations. However, it has to be noted that eqn. (13.1) is a gross simplification of the reality, because several parallel pathways are most probably involved. Note that e.g. in a detailed analysis of cellulose degradation products obtained under anaerobic conditions at high temperatures in NaOH solutions, up to 65 reaction products (mainly hydroxy monocarboxylic and dicarboxylic acids) were detected (NIEMELÄ & SJÖSTRÖM, 1986, NIEMELÄ, 1987). Other feasible reaction products than those shown in eqn. (13.1) would be short-chain aliphatic alcohols, e.g. from Cannizzaro-type disproportionation of aldehydes. However the products may not contain vicinal hydroxo groups, otherwise these would be detectable in HPAEC, where no such peaks were observed. Further, these alcohols may be oxidised forming short-chain aliphatic carboxylic acids as those shown in eqn. 13.1.

With respect to the question of possible reaction partners under anaerobic conditions one may only speculate on possible reaction partners contained in Ca(OH)$_2$ or HCP (cf. ISA.1008, ISA.1009):
• Traces of $O_2$ sorbed to the solid that are not removed during the evacuation procedure in the lock of the glove box and remain bound to the solid under the $N_2$ atmosphere. Although there is no direct evidence for such an idea, it might explain the seeming difference between results in ISA.1003 and e.g. ISA.1007 or ISA.1009. The amount of $O_2$ bound to $Ca(OH)_2$ may be different depending on the exact procedure during posting the substances into the glove box. During the time when experiments ISA.1005 – ISA.1011 were carried out, special care was taken to "acclimatise" the substances to the box atmosphere, whereas less attention was paid in previous experiments to this measure of precaution. Finally note that diffusion of traces of $O_2$ from the glove box atmosphere into the reaction vessels cannot explain the observed rates of transformation of $\alpha$-ISA (cf. the discussion in chapter 7).

The hypothesis of traces of $O_2$ bound to the solids could also explain, why a quantitative conversion of $\alpha$-ISA to reaction products was observed in some of the tests in experiment ISA.1001. In those experiments only the headspace of the suspensions was flushed with argon. Consequently it can be expected that the amount of $O_2$ bound to $Ca(OH)_2$ may be much larger than in $Ca(OH)_2$ brought into the glove box. Such $Ca(OH)_2$ would thus have a smaller capacity for turnover of $\alpha$-ISA than $Ca(OH)_2$ in an argon-flushed suspension.

The rates of turnover observed in experiment ISA.1009 (orders of 2 months for completion) are not in contradiction with those observed e.g. in experiment ISA.1005 or ISA.1011 (orders of days), because $O_2$ needs to reach the reactive sites when added to the headspace, whereas it would already be present in $Ca(OH)_2$, if the present hypothesis applies.

• The reaction partner is present as an impurity in $Ca(OH)_2$. Using the rule-of-thumb of 1 µmol of $\alpha$-ISA being converted per gram of $Ca(OH)_2$, one may speculate on the amount of such an impurity, without knowing the stoichiometric relationship between the reaction partners. For a rough estimate it may be sufficient to assume that 4 electrons are needed to convert $\alpha$-ISA (cf. eqn. (13.1)) to reaction products and that the unknown reaction partner would be oxidised in a 1 electron step. When further assuming that the unknown reaction partner has an atomic weight of 60 g mol$^{-1}$, the stoichiometric equivalent of the unknown reaction partner for conversion of 1 µmol of $\alpha$-ISA would be 4 µmol, or 0.24 mg of the unknown reaction partner. Consequently the content of impurity in $Ca(OH)_2$ would be 240 mg kg$^{-1}$. According to the information of the manufacturer, Fe is a main impurity in $Ca(OH)_2$ present at
< 500 mg kg\(^{-1}\). It is a general experience that the actual contents fall far below these declarations. However the hypothesis of an impurity cannot simply be dismissed by such an argumentation. A much more severe argument against this hypothesis is again the inconsistency for the extent of turnover between ISA.1003 and other experiments. For many of these experiments Ca(OH)\(_2\) was used from the same bottle. There is no evident explanation that the amount of impurities should be so different in various experiments.

Finally the conclusions are put in the light of the project's aims and history. The aims given in the Introduction may be detailed as follows:

1. To investigate the chemical reactivity of \(\alpha\)-ISA in suspensions of Ca(OH)\(_2\) as a model system.

2. To investigate the chemical reactivity of \(\alpha\)-ISA in suspensions of crushed hardened cement paste.

3. To test whether the knowledge gained with the Ca(OH)\(_2\) system can be transferred to the cement system.

4. To identify the degradation products either with respect to their structure or influence on radionuclide speciation under repository conditions.

5. To possibly make predictions for the long-term stability of \(\alpha\)-ISA in the environment of a cementitious repository for radioactive waste.

Objectives #1 – #3 were reasonably met. As it turned out in the course of the project that \(\alpha\)-ISA was not quantitatively converted to fragmentation products under relevant repository conditions, objective #4 became obsolete. The strategy of the project had to be reoriented, and the focus of the work was rather laid on the questions of (i) the reasons for stopping of the reaction and (ii) the role of O\(_2\) in the transformation of \(\alpha\)-ISA. Both questions found an answer in experiments ISA.1008 and ISA.1009. Objective #5 was reached in the sense that there are no reasons to assume that \(\alpha\)-ISA will be converted to fragmentation products within "short time" (on the repository time scale).
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