

PAPER II

TEIR, S., ELONEVA, S., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2007. Dissolution of
Steelmaking Slags in Acetic Acid for Precipitated Calcium Carbonate Production.

Energy, 32(4), 528-539.

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Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production

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Received 27 October 2005

Abstract

A promising option for long-term storage of CO₂ is to fixate carbon dioxide as magnesium- and calcium carbonates. Slags from iron and steel works are potential raw materials for carbonation due to their high contents of calcium silicates. Precipitated calcium carbonate (PCC) is used as filler and coating materials in paper. If slag could be used instead of limestone for producing PCC, considerable energy savings and carbon dioxide emissions reductions could be achieved. In this paper, the leaching of calcium from iron and steel slags using acetic acid was investigated. Thermodynamic equilibrium calculations at atmospheric gas pressures showed that extraction of calcium is exothermic and feasible at temperatures lower than 156 °C, while the precipitation of calcium carbonate is endothermic and feasible at temperatures above 45 °C. The formation of calcium- and magnesium acetate in the solution was found to be thermodynamically possible. Laboratory-scale batch experiments showed that iron and steel slags rapidly dissolve in acetic acid in a few minutes and the exothermic nature of the reaction was verified. While silicon was successfully removed by filtration using solution temperatures of 70–80 °C, further separation methods are required for removing iron, aluminum and magnesium from the solution.

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Keywords: Mineral carbonation; CO₂ storage; CO₂ utilization; Steel slag; Calcium carbonate; Calcium silicate

1. Introduction

The increasing carbon dioxide, CO₂, content in the atmosphere and its long-term effect on the climate has led to increasing interest and research in options for capture, utilization and long-term storage of carbon dioxide. Oil refineries, coal-fired power plants, iron and steel works, cement, lime and natural gas production are the largest concentrated sources of anthropogenic CO₂ emissions. The current potential to reuse CO₂ in industry is limited, so most of the captured CO₂ would have to be stored. Although CO₂ can be stored in aquifers and utilized in depleted oil and gas fields, the distances to the CO₂ producer site can be thousands of kilometers, which raise the overall storage costs significantly.

The disposal of CO₂ as solid carbonates is another potential option for long-term storage of CO₂. This method accelerates the natural weathering of silicate minerals, where these minerals react with CO₂ and form carbonate minerals and silica [1]. Suitable carbonates for storing CO₂ are magnesium- and calcium-based carbonates, since they are hard to dissolve in water. While magnesium- and calcium oxides and hydroxides carbonate faster, the availability of magnesium- and calcium silicates is much better [2]. Although calcium silicate has been successfully carbonated at temperatures and pressures relevant for industrial processes [3], natural calcium silicate resources are too small and expensive to be of practical interest [2,4]. Therefore, current research activities focus mostly on carbonation of magnesium silicates [5]. However, industrial by-products, such as iron and steel slags and cement-based materials, can have very high contents of calcium and magnesium oxides, and could therefore be carbonated for CO₂ storage and hazardous waste

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neutralization [6–8]. At the same time, calcium carbonate (CaCO_3) and precipitated calcium carbonate (PCC) is currently far more industrial uses than magnesium carbonate.

We are currently studying the possibility to produce calcium carbonates by leaching calcium from calcium silicates using acetic acid, and precipitating calcium carbonate out of the solution by injection of CO_2 . In this paper, we have focused on the extraction of calcium from iron and steel slag in aqueous solutions of acetic acid.

2. Concept

Currently, PCC is manufactured by carbonating calcined limestone (natural calcium carbonate). However, the calcination process produces more CO_2 than is bound during the carbonation process. A process that produces PCC from a carbonate-free mineral would therefore be a more environmentally sustainable method for producing PCC, since no calcination step would be required. However, producing calcium carbonates from calcium silicates requires a more complex process and no commercial process is currently available. Natural calcium silicates, such as wollastonite, are too rare and expensive to be used for producing PCC [4]. Instead, iron and steel slag could provide a suitable feedstock for PCC production, since slags are free from carbonates and have high contents of calcium.

2.1. Iron and steel slags

Iron and steel slags (or steelmaking slags) are non-metallic by-products from iron and steel manufacturing, and consist primarily of calcium, magnesium, and aluminum silicates in various combinations. Slag is formed when limestone reacts with silicon dioxide and other impurities of iron ore at high temperatures. Different blast furnace slag types are produced depending on cooling technique used: air-cooled, expanded or foamed, granulated, or pelletized slag. Iron and steel slags are highly variable with respect to their composition, even for the same plant and furnace [9]. The amount of slag produced is largely related to the overall chemistry of the raw material. It has been estimated that the world output in 2003 was 160–200 Mt of iron slag and 96–145 Mt of steel slag [10]. Iron and steel slags are mainly utilized as a concrete aggregate and in various applications in highway construction.

In Finland, there are four steel plants in operation that produce in total 1.4 Mt of slag/year [11]. Most of the Finnish steelmaking slags have a high concentration of calcium oxide (CaO) similar to that of wollastonite. Several slags have a high content of magnesium oxide (MgO) as well. Iron and steel slag also contains several trace elements, which may be freed if the slags are dissolved in a carbonation process.

Steel slags have recently been found to carbonate easily under mild process conditions. Huijgen et al. [8] reached

calcium conversions of 70% in 30 min with steel slag in distilled water at 20 bar CO_2 pressure and a temperature of 200 °C. However, carbonating iron and steel slags in a single step will produce a slurry containing all carbonates, silica and other impurities from the slag. Multi-step processes, such as those suggested by Yogo et al. [12] and Kakizawa et al. [3], may be better alternatives for separating various elements at different stages and producing a purer carbonate product.

2.2. Current PCC production process

Most PCC is currently produced from lime, which has been manufactured by calcining limestone in a lime kiln at temperatures over 900 °C:



The lime (calcium oxide) is hydrated with water into a calcium hydroxide slurry:



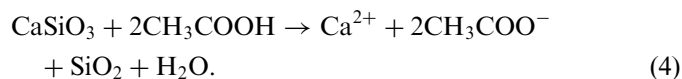
CO_2 is injected into the slurry, where it reacts with calcium hydroxide (Ca(OH)_2) and forms calcium carbonate, which precipitates out:



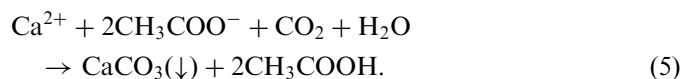
The process can utilize process or power plant flue gases as such to satisfy its CO_2 requirements. Although CO_2 is bound during the PCC production process, a larger amount of CO_2 is released from the lime production, due to the fuel combusted to provide heat to the endothermic calcination reaction (Eq. 1) [4].

2.3. Alternative carbonation process

One of the most promising multi-step process ideas for producing calcium carbonate from calcium silicates is the acetic acid carbonation process suggested and studied by Kakizawa et al. [3]. The process consists of two main steps, where the reactions occur (Fig. 1). First, calcium ions are extracted from a natural calcium silicate mineral by leaching in acetic acid (CH_3COOH):



After filtrating silica out of the solution, CO_2 is pumped into the solution, forming calcium carbonate that precipitates from the solution:



Acetic acid is recovered in this step and recycled for use in the extraction step. According to Kakizawa et al., the Gibbs free energy change of each step is negative, and should therefore not require large amounts of energy input. However, the second step may require pressurized CO_2 in order to achieve a higher carbonation efficiency.

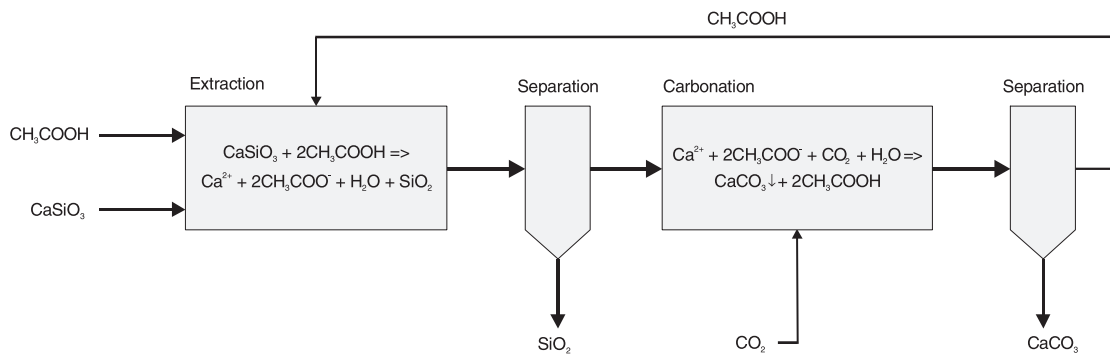
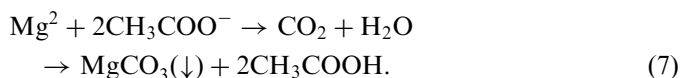
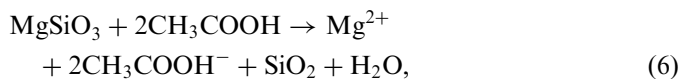


Fig. 1. Multi-step process for carbonating calcium silicates using acetic acid.

Kakizawa et al. studied the process with batch experiments. Using an aqueous solution of acetic acid (27% acid and 72% water at 60 °C) to extract calcium ions from wollastonite (CaSiO_3) an extraction ratio of 48% was achieved in 250 min. Using CO_2 pressures of 5–50 bar and temperatures of 40–80 °C, a carbonate conversion of 20% from a solution of calcium acetate and water was achieved in approximately 1 h [3]. However, the composition of the precipitate was not studied.

This process could possibly be used for carbonating iron and steel slags as well, since the composition of several slag types resemble wollastonite [11]. However, iron and steel slag can also have high contents of magnesium silicates (and many other compounds), for which it is possible that similar reactions might occur in contact with acetic acid:



For instance, 3.1 kg of blast furnace slag can store 1 kg of CO_2 assuming a stoichiometric conversion of the CaO contained in the slag [11]. If also the MgO components of the blast furnace slag could be carbonated, the slag requirements would be reduced to 2.3 kg/kg CO_2 . However, there are also small contents of many other compounds in iron and steel slag (such as heavy metals) which may be released by acetic acid.

2.4. Process comparison

We have studied the feasibility of producing calcium carbonates using natural calcium silicates by process modeling, and compared it with the current PCC production route from limestone in a previous paper [4]. The net CO_2 emissions from the current PCC production method were according to our model 0.21 kg CO_2 /kg CaCO_3 produced, with the CO_2 bound in the carbonation process accounted for, and the energy need for the calcination facility included. The alternative carbonation process binds 0.44 kg CO_2 /kg CaCO_3 produced, but the power demand for the process, modeled to run at 30 bar CO_2 pressure,

causes indirectly 0.10 kg CO_2 /kg CaCO_3 from (fossil fuel-based) power generation, reducing the net sequestration of CO_2 to 0.34 kg CO_2 /kg CaCO_3 , which is still a significant reduction (according to Kakizawa et al. the best precipitation rate was achieved at 30 bar CO_2 pressure). If the alternative carbonation process could be developed to produce synthetic CaCO_3 the emissions from energy intensive lime kilns producing CaO for PCC production could also be omitted. This would reduce the total CO_2 emissions of the PCC production chain by a further 0.21 kg CO_2 /kg CaCO_3 to a total of 0.55 kg CO_2 /kg CaCO_3 produced. Therefore, the acetic acid process seems to have a high potential for simultaneously reducing CO_2 emissions and producing PCC. Although natural calcium silicates were found to be too expensive for use as feedstock for the process [4], steelmaking slags were found to be much cheaper [11]. However, the possibility to use steelmaking slags as feedstock for this process has not previously been studied.

2.5. Potential and profit margins

We have recently studied the potential for reducing CO_2 emissions by carbonating iron and steel slag [11]. Using iron and steel slag from Finnish steel mills, 0.26–0.53 kg of CO_2 could be stored/kg of slag carbonated (taking both the CaO and MgO content of the slags into consideration), reducing the CO_2 emissions of the steel mills by 8–21%. The maximum potential for reducing CO_2 emissions by slag carbonation for the four steel mills in Finland was calculated to be 550 kt/a CO_2 , while the world-wide potential was estimated to be 70–180 Mt CO_2 /a (calculated using composition data of Finnish slags). Production of PCC from carbonation of iron and steel slag could be a more profitable refining method for the slag products, if the purity required for commercial PCC could be achieved. In Finland, granulated blast furnace slag can be purchased for 10 €/t, which is approximately the same price as for limestone lumps used for producing lime for PCC manufacturing (11 €/t), while the cheapest available PCC type has a price tag of 120 €/t. Since only the CaO-component of the slag is used for PCC production, the CO_2 reduction potential is lower than for carbonation of both

CaO and MgO in slag. Using the alternative carbonation process for PCC production, roughly 290 kt CO₂ emissions per year could be avoided from the steel factories in Finland, while the annual output of PCC would be 850 kt [11].

Although calcium carbonate is a stable compound, which is thermodynamically favored over CO₂ and sparingly soluble in water, waste incineration of products containing PCC may eventually release the CO₂ stored as carbonate. However, if PCC produced from slag could replace other PCC products produced from lime, the omission of using a lime kiln for calcination would reduce CO₂ emissions and save natural mineral resources regardless of the means for disposal of PCC.

3. Methods

The alternative carbonation process had not been previously tested for steelmaking slags. Also, the elemental composition of the filtered solids from the crystallization experiments by Kakizawa et al. had not been reported. Therefore, we performed simple thermodynamic equilibrium calculations prior to laboratory experiments to determine if calcium could be extracted from steelmaking slags using acetic acid. We also wanted to verify that calcium carbonate and magnesium carbonates are theoretically possible products of the process. The thermodynamic equilibrium of reaction equations Eqs. (4)–(7) and the solution equilibrium of blast furnace slag was calculated using Outokumpu HSC 5.1. The program uses minimization of total Gibbs energy (G) of the compounds involved for determining chemical compositions at thermodynamic equilibrium. The calculations were only performed for carbonation at atmospheric pressure using the main elements of blast furnace slags (data of average blast furnace composition supplied by Ruukki) as input data.

The iron and steel slags used in our experiments were provided by Raahe steel works (Ruukki) and Tornio steel works (Outokumpu). Wollastonite mined near Lappeenranta (Nordkalk) was also used for comparison. Materials with a large size distribution were sieved to 125–500 μm and only the sieved fractions were studied, while materials in powder form were used as such. The composition of the calcium silicate-based materials used in the experiments were analyzed using X-ray fluorescence spectroscopy (XRF). Crystallite orientations of the samples were determined by X-ray diffraction (XRD). In order to determine more exact elemental concentrations of steel slags and their variation, three samples of each material were separately dissolved in a standardized solution of hydrochloric acid, hydrofluoric acid, and phosphoric acid. Saturated boric acid was later added to each batch of solution for complete dissolutions of the materials. The solutions were analyzed using Inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The extraction of calcium ions from various iron and steel slags in acetic acid was studied using batch experiments. The experimental setup is displayed in Fig. 2. Acetic acid solutions of various concentrations were heated to a specified temperature in a glass reactor of 250 ml. The glass reactor was surrounded by a water bath, which was heated using a separate closed temperature-controlled water bath with an external water flow connected to the open water bath containing the reactor. Nitrogen was continuously fed to the reactor (above the surface of the solution) at 1 l/min to prevent CO₂ in air from interfering with the experiments. The solution was stirred using a magnetic stirrer at approximately 600–700 rpm. When the temperature for the solution had stabilized after heat-up to the desired temperature, 4.2 g of slag was added to the solution (in order to be comparable with previous experiments made with 300 ml solution and 5 g of slag [13]). The temperature

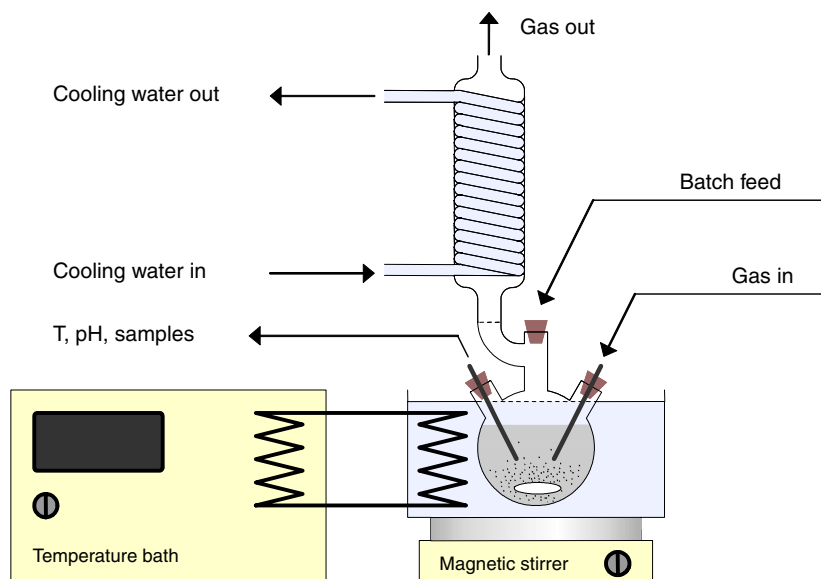


Fig. 2. Experimental setup.

and pH of the solution were recorded with electrodes inline, and were not regulated after the addition of the batch. The solution was stirred for 2 h, and four samples of 10 ml each were extracted 5, 20 min, 1, and 2 h after the addition of the slag using a syringe. The samples were immediately filtered through a syringe membrane filter of 0.45 μm pore size and the liquid samples were sent to analysis. In order to estimate the losses due to evaporation, the weight change of the solution was calculated by measuring the reactor weight before and after the experiment run. The mass changes from addition of the slag batch and the sample extraction were also accounted for. The weight change of the solution is referred to as “mass balance check” in the result section.

Based on the results from the XRF-analysis the concentrations of the five main common elements of the materials in the solution samples were measured after the tests using ICP-AES and atomic absorption spectrophotometry AAS. Two different dilutions were prepared from each solution sample, and the concentrations of the selected elements in each dilution were measured using two separate frequencies. The accuracy of the ICP-AES and AAS analyses were estimated to $\pm 2\%$. The solution was assumed to be free from these elements prior to the addition of the batch of slag, being prepared from only distilled water and pure acetic acid.

4. Results and discussion

4.1. Thermodynamic equilibrium calculations

Gibbs free energy calculations of the extraction reactions (Eqs. (4) and (6)) using HSC 5.1 showed that the extraction of Ca^{+2} -ions from CaSiO_3 is thermodynamically possible at temperatures lower than 156 $^\circ\text{C}$, while the extraction of Mg^{+2} -ions from MgSiO_3 proceeds at temperatures lower than 123 $^\circ\text{C}$ (Fig. 3). Gibbs free energy calculations of the carbonation reactions (Eqs. (5) and (7)) showed that the carbonation of Ca^{+2} -ions proceeds already at temperatures over 45 $^\circ\text{C}$, while the carbonation of Mg^{+2} -ions should only be possible at temperatures over 144 $^\circ\text{C}$. The

calculations also show that the extraction reactions are exothermic ($\Delta H < 0$), while the carbonation reactions are endothermic ($\Delta H > 0$). The net reactions of calcium silicate carbonation (Eqs. (4) and (5)) and magnesium silicate carbonation (Eqs. (6) and (7)) are both exothermic.

The dissolution of the various species of blast furnace slag in acetic acid was studied in more detail by calculating the chemical composition at thermodynamic equilibrium using HSC. The input parameters were set to simulate the extraction experiments carried out later on, using 4.2 g of blast furnace slag in a 250 ml aqueous solution of acetic acid (33.3 wt% CH_3COOH , 66.7 wt% H_2O). Only the six largest species in blast furnace slag were used as input data, to simplify the results. All the compounds in the database of HSC 5.1 were used as potential products, except for C, C_xH_y , and all carbonates, which are unlikely products from the extraction process performed in absence of CO_2 . The results and input data are summarized in Table 1. The results show that all compounds (except for Ti) are expected to be dissolved in the solution. A large part of the metals dissolved are expected to form acetates, such as magnesium acetate, calcium acetate, and iron(II) acetate. Although Fe, S and Ti are in oxide states in slags, having the input of these in elemental form does not notably affect the outcome of the calculation, since HSC merely calculates the equilibrium composition. Although all compounds are not likely to be formed due to slow kinetics, the modeling results give a hint upon the feasibility of the extraction.

4.2. Characterization of calcium-based materials used in the experiments

The XRF-analyses of the sieved fractions of the calcium silicate-based materials (Table 2) are similar to the compositional data supplied by the manufacturers. Therefore, the sieved fractions used in the experiments should well represent the materials in terms of composition. Based on the XRF-analyses Ca, Mg, Al, Fe, and Si were selected for analysis by ICP-AES. Table 3 shows results from the ICP-AES analyses of the selected elements in the

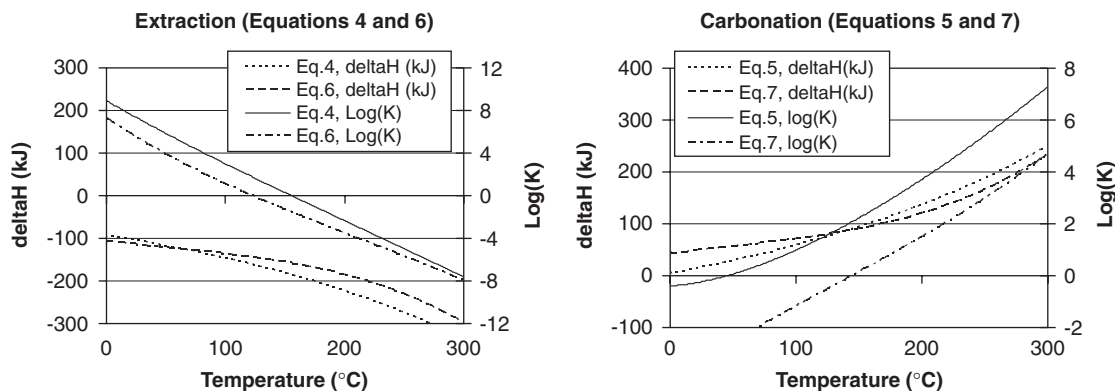


Fig. 3. Equilibrium constant K and ΔH calculated for the reactions involved in acetic acid carbonation for CaSiO_3 (Eqs. (4) and (5)) and MgSiO_3 (Eqs. (6) and (7)).

Table 1
Thermodynamic equilibrium composition of solution of blast furnace slag (six main species) in acetic acid (33.3 wt%) and water (66.7 wt%)

Input	Composition (g)	Output	Element	Composition as conversion rates of element		
				At 30 °C (%)	At 50 °C (%)	At 70 °C (%)
H ₂ O(aq)	166.7	CaCH ₃ COO ⁺	Ca	62	65	70
CH ₃ COOH(aq)	83.3	Ca ²⁺	Ca	38	35	30
CaO	1.70	Si(OH) ₃ ⁻	Si	100	100	100
SiO ₂	1.46	Mg(CH ₃ COO) ₂ (aq)	Mg	76	70	69
MgO	0.43	Mg ²⁺	Mg	24	30	31
Al ₂ O ₃	0.39	Al ₃ (OH) ₄ ⁵⁺	Al	100	100	100
Ti	0.042	TiO ₂	Ti	100	100	100
Fe	0.026	Fe(CH ₃ COO) ₂ (aq)	Fe	91	89	89
S	0.008	Fe ²⁺	Fe	9	11	11
		S ₄ O ₃ ⁻²	S	99	99	98
		S ₅ O ₃ ⁻²	S	1	1	2

The results are presented as equilibrium conversion rates of various elements.

Table 2
Composition of calcium silicate-based materials used in the experiments as determined by XRF-analysis (units: wt%)^a

Element	Blast furnace slag (350–500 μm)	Steel converter slag (350–500 μm)	Electric arc furnace slag (125–350 μm)	AOD process slag (< 125 μm)	Wollastonite (< 250 μm)
CaO	40.6	43.6	40.8	60.7	44.5
SiO ₂	34.1	13.9	26.6	27.6	52.2
Fe ₂ O ₃	0.901	24.1	1.59	0.210	0.297
MgO	10.7	1.44	7.21	5.83	0.541
Al ₂ O ₃	9.40	1.77	8.36	1.21	1.48
F	0.07	0	0.11	5.5	0.02
Cr	0.003	0.232	5.07	0.228	0.001
Ti	1.03	0.512	2.64	0.356	0.012
Mn	0.376	2.39	2.29	0.076	0.005
S	1.73	0.086	0.092	0.273	0.008

^aOnly elements present at > 1 wt% are shown.

Table 3
Concentrations of selected elements in calcium silicate-based materials used in the experiments as determined by dissolution and ICP-AES-analysis (units: wt%)^a

	Blast furnace slag (350–500 μm)		Steel converter slag (350–500 μm)		Electric arc furnace slag (125–350 μm)		AOD process slag (< 125 μm)		Wollastonite (< 250 μm)	
	Average	Std.dev.	Average	Std.dev.	Average	Std.dev.	Average	Std.dev.	Average	Std.dev.
CaO	39.0	1.58	41.4	2.21	38.9	0.583	69.4	1.07	38.8	5.20
SiO ₂	25.7	0.682	11.0	0.830	21.2	0.166	22.0	0.598	32.2	4.01
Fe ₂ O ₃	0.404	0.028	26.0	1.69	3.82	0.766	0.252	0.110	0.201	0.024
MgO	11.9	0.370	1.42	0.054	6.05	0.033	6.51	0.010	0.506	0.023
Al ₂ O ₃	8.64	0.486	1.88	0.293	6.34	0.129	1.22	0.064	1.17	0.159

^aResults expressed in terms of oxides. The standard deviation was calculated based on the results from dissolutions of three samples of each material.

dissolutions of the calcium-based materials. In order to compare the crystal structures of iron and steel slags with wollastonite, XRD analyses of the sieved fractions were made. The results from the XRD analyses have been summarized in Table 4. Phases could be identified from all materials except for the blast furnace slag sample, since its crystal structure is mostly amorphous. Calcium silicate in the form of Ca₂SiO₄ was identified both in argon–oxygen

decarburization (AOD) process slag and steel converter slag.

4.3. Extraction experiments

To compare the potential for leaching calcium out from iron and steel slags, various slags were dissolved in aqueous solutions of acetic acid (33.3 wt% glacial acetic acid and

Table 4
Minerals in calcium silicate-based materials identified by XRD

Material analyzed	Highest peak (counts)	Phases identified
Wollastonite	2500	Wollastonite CaSiO_3 , quartz SiO_2
AOD process slag	1000	Fluorite CaF_2 , periclase MgO , calcium silicate $\text{Ca}_2(\text{SiO}_4)$
Electric arc furnace slag	350	Gehlenite $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$, merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, magnesiochromite $(\text{Mg}, \text{Fe})(\text{Cr}, \text{Al})_2\text{O}_4$
Steel converter slag	300	Srebrodolskite $\text{Ca}_2\text{Fe}_2\text{O}_5$, lime CaO , iron Fe , calcium silicate Ca_2SiO_4 , calcium iron oxide $\text{Ca}_2\text{Fe}_{1.5.6} \text{O}_{2.5}$
Blast furnace slag		Mostly amorphous phases

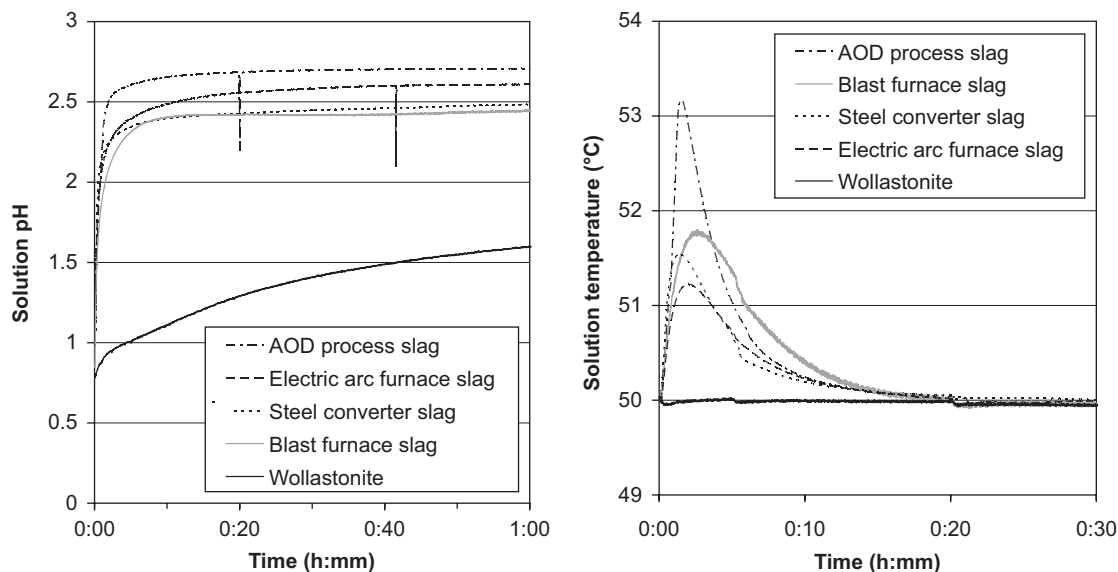


Fig. 4. Inline pH and temperature recordings of extraction experiments in aqueous solution of acetic acid (33.3%) at 50 °C (batch of 4.2 g slag added at 0:00). Peaks in pH curves at 0:20 and 0:42 were caused by temporary electrode disturbances.

66.7% distilled water, $\text{pH} = 1.5$ at 25 °C) at a solution temperature of 50 °C. When a batch of slag was added to a solution of acetic acid, the solution temperature rose briefly to 1.2–3.1 °C, indicating a reaction occurring and verifying the exothermic nature of the reaction (Fig. 4). The highest temperature peak was observed with AOD process slag. The pH of the solution rose also in 10 min after the slag addition from 0.8–1.1 to 2.4–2.7. However, no significant increase in solution temperature could be observed when adding wollastonite to a similar solution of acetic acid. The pH of the solution containing wollastonite rose very slowly from 0.8 to 1.7 during 2 h, indicating that the extraction of calcium from wollastonite is slow. The result from the AAS and ICP-AES analyses (Fig. 5) verifies that only 51% of the calcium fixed in wollastonite could be extracted during 2 h. This is similar to the results achieved by Kakizawa et al. [3], who reported that 48% of the calcium fixed in wollastonite was extracted during 250 min when dissolving 13.26 g of wollastonite in an aqueous solution of acetic acid (acetic acid/water = 13.72 g/50 g). We found the extraction of calcium from iron and steel slags to be much faster: almost all the calcium from iron and steel slag could be dissolved (Fig. 6–9), which was also predicted by thermodynamic

modeling. The extraction efficiency numbers were calculated by comparing the concentration of selected elements in the filtered solution samples with concentrations of the elements in the raw materials (Table 3) and accounting for the loss of solution volume due to sample extraction. However, the analyses also show that other elements of the slag, such as silicon, dissolve as well. Steel converter slag has, besides calcium, high contents of iron, while the other slags tested have high contents of magnesium. Electric arc furnace slag and blast furnace slag contain aluminum as well, which was released into the solution during the experiments. The extraction efficiency of blast furnace slag (Fig. 6) was found to exceed 100%. Since the mass balance shows only a loss of 3.7% (due to evaporation of the solution), the result indicates that the concentration of CaO of the blast furnace slag sample used in that experiment was higher than that of the samples analyzed in Table 3.

In order to determine the influence of acetic acid concentration in the solution, additional extraction experiments with blast furnace slag were performed with aqueous acetic acid solutions of varying concentrations: 0 wt%, 0.04 wt%, 4 wt%, 10 wt%, and 33.3 wt% acetic acid

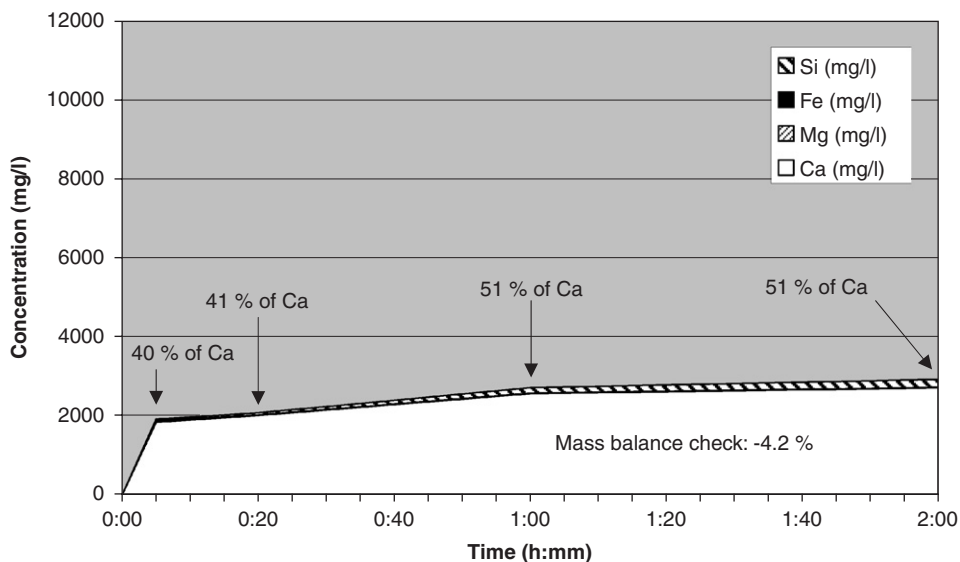


Fig. 5. Dissolution of wollastonite in an aqueous solution (250 ml) of acetic acid (33.3 wt%) at 50 °C (batch of 4.2 g added at 0:00).

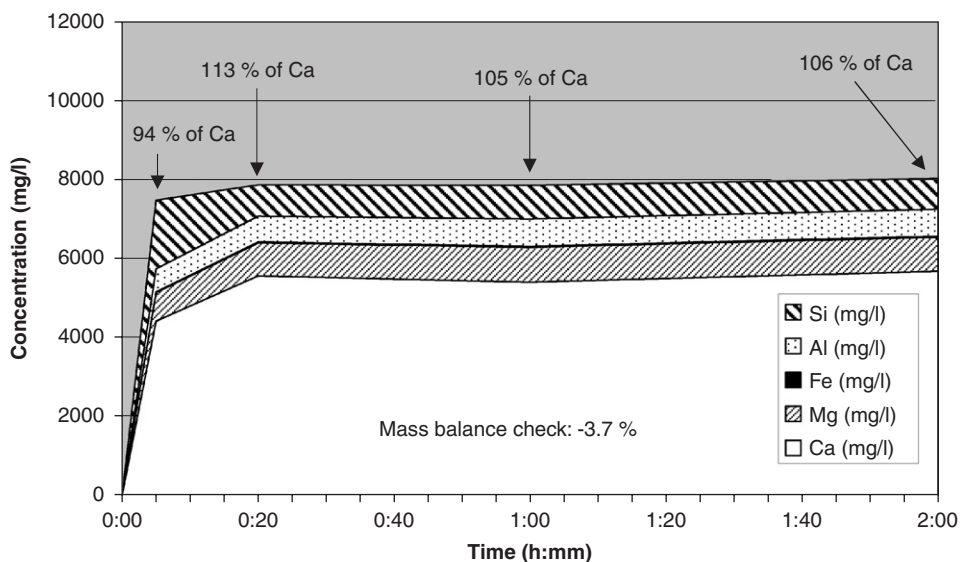


Fig. 6. Dissolution of blast furnace slag in an aqueous solution (250 ml) of acetic acid (33.3 wt%) at 50 °C (batch of 4.2 g added at 0:00).

(pH = 6.2, 3.4, 2.6, 2.3, 1.5, respectively, measured at 25 °C). The other experiment parameters were kept similar to the previous experiments. The results from the AAS and ICP-AES analyses (Fig. 10) show that the acetic acid concentration of the solution has a dramatic effect upon extraction of calcium in the range 0–10 wt% acetic acid. Only 30 mg Ca/l was extracted after 2 h of residence time in water, while 4.0 g Ca/l was extracted already in 5 min using an aqueous solution of 10 wt% acetic acid. Using a solution of 33.3 wt% acetic acid produced a result similar to the experiment performed at 10 wt% acetic acid. Almost all of the calcium in the batch of slag was extracted in a solution of only 10 wt% acetic acid, which indicates that roughly 6–7 ml glacial acetic acid is required/gram of blast furnace slag for adequate calcium extraction.

The effect of temperature upon the extraction efficiency was investigated by performing additional extraction experiments of blast furnace slags at 30 and 70 °C. A solution concentration of 4 wt% acetic acid was selected for study, since calcium was only partially extracted using this solution concentration at 50 °C (Fig. 10). The results from the AAS and ICP-AES analyses (Fig. 11) showed that temperature has a significant effect upon the solubility of calcium (and other elements as well) from blast furnace slag. At 30 °C the extraction is significantly slower than at 50 °C, but instead a better calcium extraction can be achieved. At 70 °C the extraction process is faster than at 50 °C, but less calcium can be extracted. Apparently the solubility of blast furnace slag decreases with higher temperatures. However, this can be compensated for by

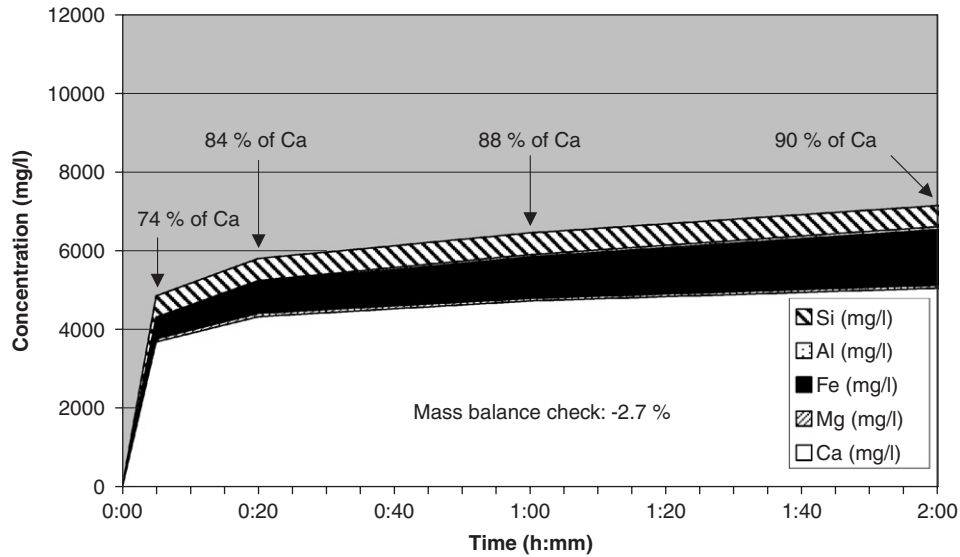


Fig. 7. Dissolution of steel converter slag in an aqueous solution (250 ml) of acetic acid (33.3 wt%) at 50 °C (batch of 4.2 g added at 0:00).

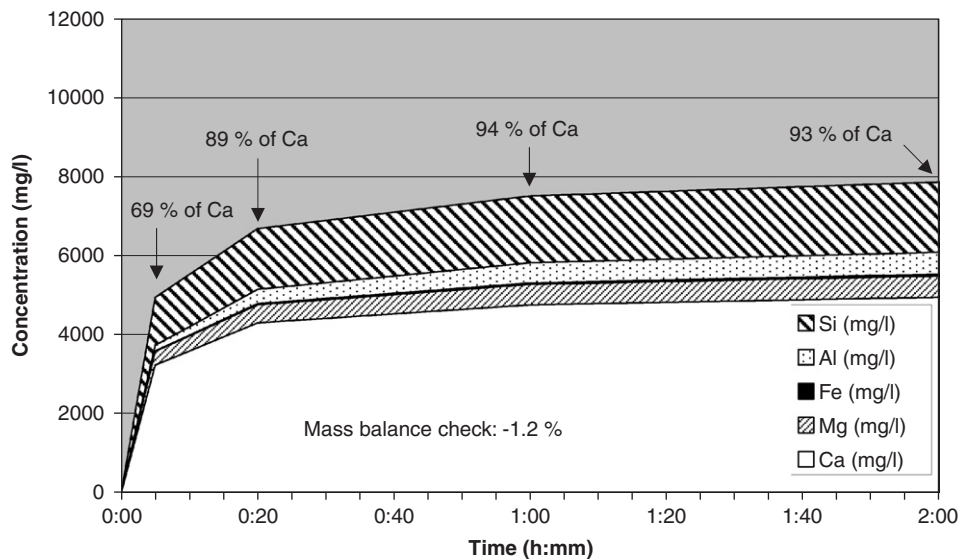


Fig. 8. Dissolution of electric arc furnace slag in an aqueous solution (250 ml) of acetic acid (33.3 wt%) at 50 °C (batch of 4.2 g added at 0:00).

increasing the acetic acid concentration in the aqueous solution.

In our previous extraction experiments we found that the dissolved silicon content of the extraction solution was significantly reduced after 1 h dissolution of blast furnace slag or steel converter slag at 70 and 80 °C in an aqueous solution of 33.3% acetic acid [13]. We observed that the silica dissolved in the solution forms a gel under these conditions, which can be mechanically filtered from the solution. To produce a solution suitable for precipitation of CaCO_3 , i.e. with high concentration of calcium but low concentration of silica, 50 g of blast furnace slag was dissolved in a mixture of 100 ml of acetic acid and 200 ml of distilled water (500 ml total reactor volume) at 70 °C for

2 h. The composition of the produced calcium-rich solution is shown in Table 5. As can be seen from the table, it is possible to minimize the content of silicon in the solutions by leaching slag at 70 °C in an aqueous solution of 33.3 wt% acetic acid, and removing the formed silicon-rich gel by mechanical filtration. However, other separation measures are needed to remove aluminum, iron, magnesium and other elements released from the slag.

5. Conclusions

Carbonation of calcium silicate-rich slags is an interesting option for simultaneously reducing CO_2 emissions and refining by-products from the industry. If the produced

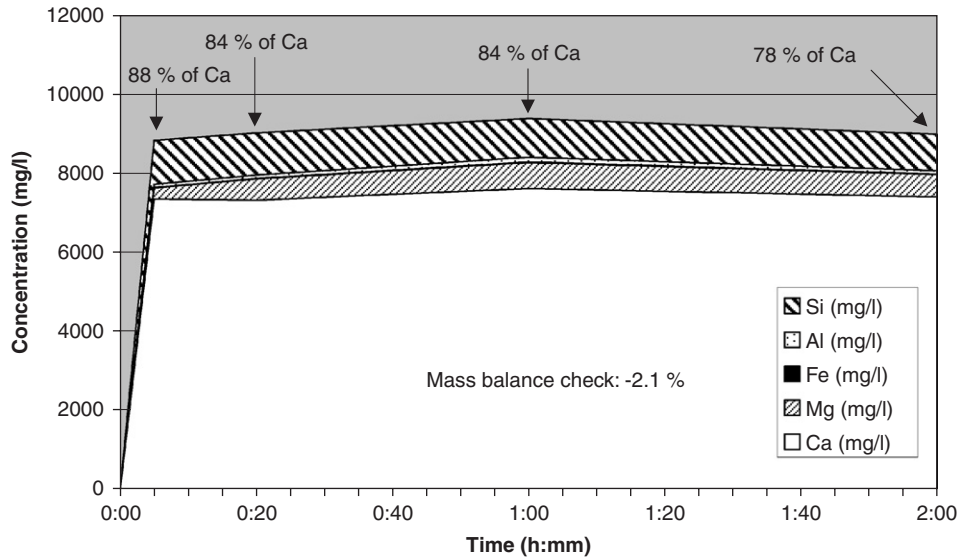


Fig. 9. Dissolution of AOD process slag in an aqueous solution (250 ml) of acetic acid (33.3 wt%) at 50 °C (batch of 4.2 g added at 0:00).

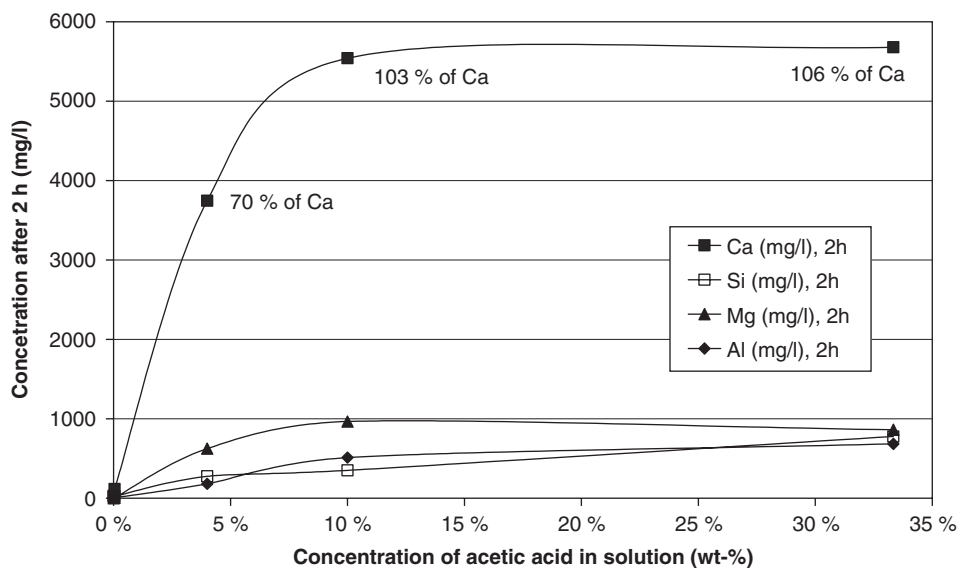


Fig. 10. Dissolution of blast furnace slag in aqueous solutions with various concentrations of acetic acid at 50 °C (batch of 4.2 g added at 0:00).

calcium carbonate could reach the purity specifications of PCC, the economic value of slags could be increased tenfold, while also reducing CO₂ emissions and preserving natural mineral resources. Although the global CO₂ storage potential by carbonating slags is low in comparison with other CO₂ storage options, it can reduce the annual CO₂ emissions for an individual steel plant with several hundreds of kilotons.

The experiments performed with extracting calcium from iron and steel slag shows that iron and steel slags dissolve more completely than wollastonite in an aqueous solution of acetic acid. While iron and steel slags dissolve poorly in water, calcium can be rapidly leached out of iron and steel slags using acetic acid. However, other elements of the

slags (such as magnesium, aluminum, iron, and silica) dissolve as well, which was predicted by thermodynamic modeling. Silicon in iron and steel slag was found to form a gel in strong acetic acid solutions (33.3 wt% acetic acid) at temperatures over 70 °C, and can be removed by mechanical filtration. Since slags dissolve easily in acetic acid, additional measures for separating other dissolved elements from acetic acid are required to reuse the acetic acid in the process. The disposal of the generated wastes will depend on in which form they can be removed from the process.

While extraction of calcium from steelmaking slags was successfully performed in acetic acid, the feasibility of the process depends on successful precipitation of calcium

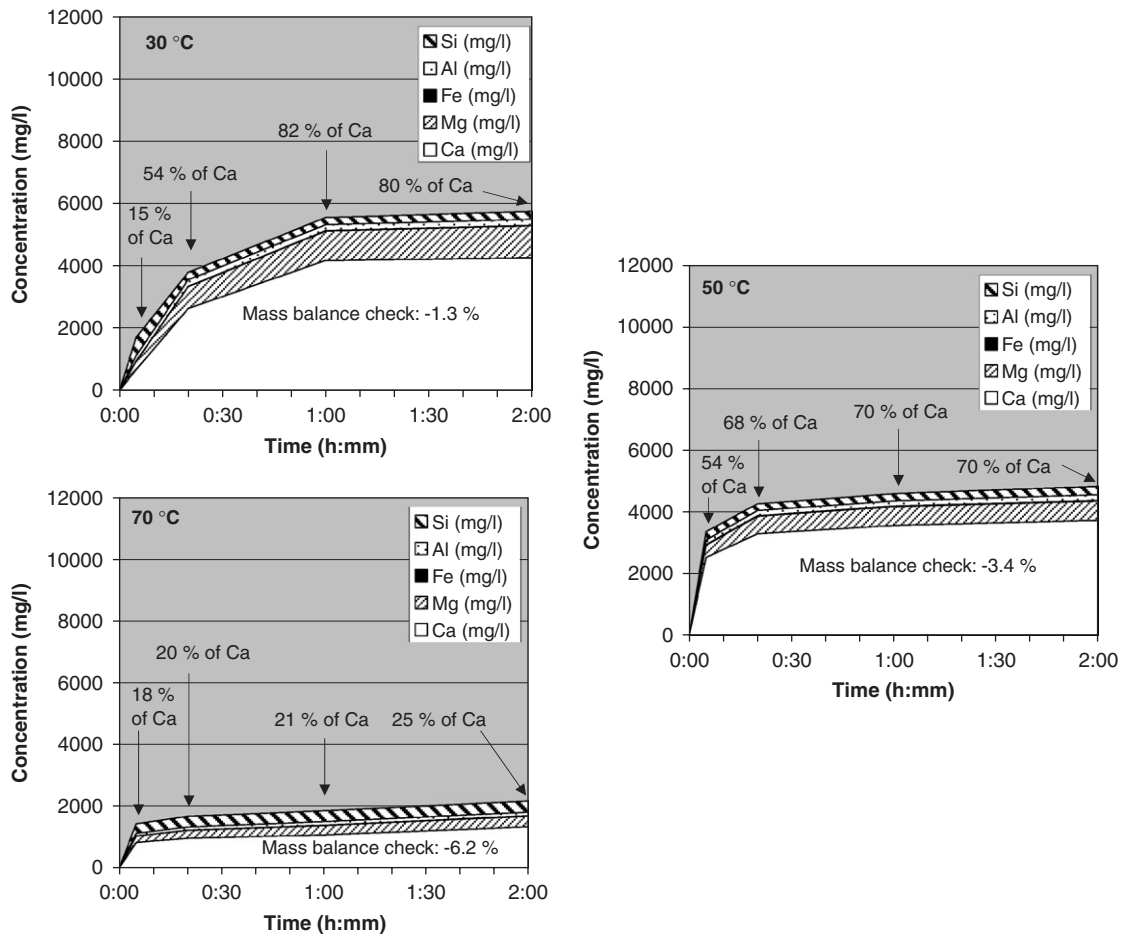


Fig. 11. Dissolution of blast furnace slag in aqueous solutions (250 ml) of acetic acid (4 wt%) at 30, 50, and 70 °C (batch of 4.2 g added at 0:00).

Table 5

Elemental composition of a filtered solution prepared at 70 °C from blast furnace slag

Al (mg/l)	Mg (mg/l)	Fe (mg/l)	Ca (mg/l)	Si (mg/l)
1218	4120	292	17000	129

carbonate. Preliminary thermodynamic equilibrium calculations predict that precipitation of CaCO_3 is thermodynamically possible over 45 °C, while the magnesium in the solution should not form carbonates at atmospheric pressures. However, to improve the conditions for successful precipitation additional methods may be required, such as pressurization or the use of additives. Future work will concentrate on the precipitation of CaCO_3 from calcium-rich aqueous solutions, as well as the removal and disposal of other elements and trace elements from the solution.

Acknowledgements

This article is based on work presented at the ECOS 2005 conference 20–22 June 2005 at Trondheim, Norway. The project was funded by Nordic Energy Research, the

Finnish Funding Agency for Technology and Innovation (TEKES), UPM, Ruukki Productions, Wärtsilä and the Finnish Recovery Boiler Committee. We thank the people working at the Laboratory of Energy Engineering and Environmental Protection and the Laboratory of Applied Thermodynamics for facilitating this work. We thank Rita Kallio at Ruukki for fast analysis services, and Petri Kobylin at the Chemical Department for his support with the HSC modeling. We also thank Hannu Revitzer at the Chemical Analysis Centre of our university for his ideas, service and support, and Ruukki, Nordkalk and Outokumpu for providing us with samples of calcium silicate-based materials. Ron Zevenhoven was Academy Research Fellow for the Academy of Finland and is currently with Åbo Akademi University.

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