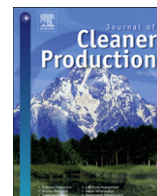


## Publication VI

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## Co-utilisation of CO<sub>2</sub> and steelmaking slags for production of pure CaCO<sub>3</sub> – legislative issues

Sanni Eloneva<sup>a,\*</sup>, Eeva-Maija Puheloinen<sup>b</sup>, Jaakko Kanerva<sup>c</sup>, Ari Ekroos<sup>b</sup>, Ron Zevenhoven<sup>d</sup>, Carl-Johan Fogelholm<sup>a</sup>

<sup>a</sup> Department of Energy Technology, Aalto University School of Science and Technology, Sähkötietäntie 4, 00076 Aalto, Finland

<sup>b</sup> Faculty of Law, University of Helsinki, Yliopistonkatu 3, 00014 Helsinki, Finland

<sup>c</sup> Department of Surveying, Aalto University School of Science and Technology, Otakaari 1, 00076 Aalto, Finland

<sup>d</sup> Thermal and Flow Engineering Laboratory, Åbo Akademi University, Piispankatu 8, 20500 Turku, Finland

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### ABSTRACT

The steel industry is characterised by large amounts of CO<sub>2</sub> emissions, but there is no easy means to reduce these emissions. One interesting option for the reduction of CO<sub>2</sub> emissions could be the utilisation of steelmaking slags for carbon dioxide mineralisation. In this option CO<sub>2</sub> is bound with the calcium of the slag material, producing stable carbonate as an end product. The utilisation of steelmaking slags as the raw material for carbon dioxide mineralisation will change the quality of the slags. If, however, this change degrades the slags it could prevent the use of slags in carbon dioxide mineralisation or make it very expensive.

The purpose of the research presented here is to evaluate this issue with the help of a case study where the quality of the residual slag from the recently suggested carbonation method was experimentally investigated. The CO<sub>2</sub> mineralisation method, based on steelmaking slags and ammonium salt solutions, was found to change the quality of the slags: the calcium content was reduced, the CaO and Ca(OH)<sub>2</sub> phases were completely dissolved, and the solubility of the V and Cr increased notably. This residual slag would presumably have to be handled as waste. Currently, the steelmaking slag used in the case study is defined as a by-product, but if it is used for CO<sub>2</sub> mineralisation instead of liming its legal status will be re-evaluated. Subsequently, the CO<sub>2</sub> mineralisation process could possibly be defined as an end-of-waste procedure.

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### 1. Introduction

The steel industry is one of the biggest sources of industrial carbon dioxide (CO<sub>2</sub>) emissions, accounting for about 7% of the total anthropogenic CO<sub>2</sub> emissions to the atmosphere (Kim and Worrell, 2002). The reduction of these emissions for climate change mitigation will not be easy, because the industry is heavily dependent on either electricity or coal. Most steel is produced either via the integrated process route or via the electric arc furnace route. In the integrated process route coal is used as reducing agent to produce molten iron, which is used to manufacture steel, producing substantial amounts of CO<sub>2</sub>. In the electric arc furnace route electricity is used to melt recycled steel into the end product. A large part of the world's electricity generation is based on fossil fuels, producing substantial amounts of CO<sub>2</sub>.

One interesting option for the reduction of CO<sub>2</sub> emissions proposed in the literature is the utilisation of steelmaking slags for carbon dioxide mineralisation (Huijgen et al., 2005; Teir et al., 2007). In this proposed option, carbon dioxide is bound with the calcium of the slag material, producing a stable carbonate as an end product. Either acidic conditions or high temperatures (~900 °C) would be required to release CO<sub>2</sub> from its carbonate form, i.e. carbon dioxide mineralisation is a very safe CO<sub>2</sub> storage option. CO<sub>2</sub> mineralisation is currently mainly at the level of laboratory-scale research, providing an alternative to the underground storage of pressurised CO<sub>2</sub>. The development of the technology is ongoing or being started at a rapidly increasing number of locations worldwide. Among the suitable raw materials for mineral carbonation, natural calcium and magnesium silicates clearly hold the greatest CO<sub>2</sub> storage capacity, while industrial waste and by-product materials, such as steelmaking slags, are more reactive. If calcium could be selectively extracted from the slags prior to carbonation, the end product could be a pure and thus also marketable calcium carbonate.

\* Corresponding author. Tel.: +358 9 470 22847; fax: +358 9 470 23418.  
E-mail address: [sanni.eloneva@tkk.fi](mailto:sanni.eloneva@tkk.fi) (S. Eloneva).

Steelmaking slags can be used for many purposes, such as raw material for road construction. However, there is not always an economically reasonable way to utilise them, or they do not fulfil the increasingly tightening environmental regulations and thus they end up being stockpiled or, in the worst case, landfilled. The legal status of the steelmaking slag material in question is likely to have an effect on the possibility of using steelmaking slag as a raw material for carbon dioxide mineralisation, especially if this use can affect the legal status of the slag. The utilisation of steelmaking slags as a raw material for carbon dioxide mineralisation will change the quality of the slags. If this change degrades the slags, it could prevent the use of slags in carbon dioxide mineralisation or make it very expensive. The purpose of the research presented here is to evaluate this issue. Therefore a case study is performed in which the quality of the residual slag from the recently suggested carbonation method (Eloneva et al., 2009) is experimentally investigated. The slag used in these experiments is steel converter slag from Ruukki's Raahe Works in Finland (the largest steel plant in the Nordic countries). A short review of the waste and by-product legislation in the European Union, and particularly in Finland, is provided.

## 2. Steelmaking slags

Steelmaking slags are generated in the steel manufacturing process. These slags can be divided into two main types; blast furnace slag and steel slag. In the blast furnace, iron ore is reduced to molten iron using coke as a reducing agent (NSA, 2009a). Lime, in the form of flux stone (limestone or dolomite) or sinter (manufactured from the iron ore and limestone) is also added to the furnace, forming blast furnace slag as it reacts with the impurities of the iron ore (mainly silica). Steel is produced from iron, scrap, and lime, either in a basic oxygen furnace or in an electric arc furnace (NSA, 2009b). In the former, oxygen is blown into the furnace to burn off the carbon, thus producing steel. In an electric arc furnace, electricity is used to melt scrap metal into steel. In both cases, steel slag is generated simultaneously with the steel as lime reacts with the impurities. These slags are generally named after the process they are generated by. Besides basic oxygen furnace slag (also called steel converter slag) and electric arc furnace slags, the generation of desulphurisation and ladle slag during the steel manufacturing is also quite likely.

Slags are removed from the processes in their molten phase and then cooled down before crushing and screening. While the chemical properties of the slags are dependent on the compositions of the raw materials and the process step they are generated in, the physical characteristics vary according to the slag processing. Blast furnace slag contains mainly calcium, aluminium, and magnesium in the form of silicates, while the principal constituents of steel slags are calcium silicates, calcium aluminoferrites, and fused oxides of calcium, iron, magnesium, and manganese (Lewis, 1982). Steel slags usually also include free calcium oxide. Additionally, when blast furnace slag is rapidly cooled down by using large quantities of water, i.e. granulated, glass-like particles are formed.

Both blast furnace slag and steel slag can be used to replace aggregates in various kinds of construction applications (NSA, 2009a,b). Steel slags are also suitable as a source of iron and flux materials in blast furnaces (Lewis, 1982) and for improving soil quality in agriculture (NSA, 2009b), while granulated blast furnace slag can even be used as a partial replacement for, or additive to, Portland cement (Rao, 2006a). Free oxide phases in steel slag can cause expansion, restricting their use in construction applications requiring very stable conditions (Rao, 2006b). The possible leaching of heavy metals can also restrict the utilisation of steelmaking slags (Rao, 2006b).

Finland has a large steel industry sector with four steelmaking plants in operation. Those plants produced a total of about 4.8 Mt of steel in 2004 (Teir, 2008). Most of the steel manufactured in Finland, produced at the Ruukki mill in Raahe and the Ovako Steel mill in Koverhar, is manufactured from iron ore and recycled metal via the integrated process route. The Ovako Steel mill at Imatra manufactures steel from scrap metal with an arc furnace process. In addition, the Outokumpu mill, situated in Tornio, uses recycled metal and ferrochrome to manufacture stainless steel. Together these mills produce approximately 1.6 Mt of steelmaking slags per year (Rinne, 2008).

## 3. Waste and by-product legislation

### 3.1. European Union

The European Union adopted a new Waste Directive on 19 November 2008 (Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives). According to the Waste Directive, EU member states are to implement the Directive by 12 December 2010. The Waste Directive sets the basic concepts and definitions related to waste management and lays down the principles for waste management. Furthermore, and what is important for the purposes of this article, the Directive clarifies the definition of waste by introducing definitions of by-product and end-of-waste status.

Lately the waste legislation in the EU has been under growing pressure to adjust to a new environment of side-products, recycling, production residues, and new technology. In theory it is clear what is or is not waste, since the definition of waste is set down in Article 3 of the Waste Directive. According to the definition in point (1) of Article 3, waste means "any substance or object which the holder discards or intends or is required to discard". Additionally, hazardous waste is defined in the Waste Directive; according to point (2) of Article 3, hazardous waste means waste which displays one or more of the hazardous properties listed in Annex III, such as being ecotoxic. The List of Waste set out in Commission Decision 2000/532/EC indicates what waste and hazardous waste are.

Putting the definition of waste into practice causes difficulties both for the competent environmental authorities and businesses. The difficulties may appear in the form of legal uncertainty, administrative costs, or internal market disturbance (COM/2005/666 final). However, the European Court of Justice (ECJ) has interpreted the definition in its decisions (ECJ decisions, 1997–2002). The ECJ has created some guidelines that are now included in the new Waste Directive. Prior to the Waste Directive, the guidelines were adopted into a Commission communication on waste and by-products (COM/2007/59 final), and these guidelines are included in the new Waste Directive, too. The two most important reforms in the Waste Directive are the definition of a by-product and end-of-waste status.

Article 5 of the Waste Directive deals with non-waste by-products. The article defines a by-product as a substance or an object, resulting from a production process, the primary aim of which is not the production of that item. A by-product may be regarded as not being waste only if four conditions are met. First, the use of a by-product must be direct, without any further processing other than normal industrial practice. The second condition is that a by-product is produced as an integral part of a production process. The third and fourth conditions relate to the further use, which has to be lawful and certain. Moreover, a common condition for by-products is the requirement of consistency with the leading principles of the EU waste policy – protection of the environment and human health. This requirement is applied when making a decision as to whether or not a substance or object is waste.

In the previous paragraph the result of a production process was not defined as waste at all if all the conditions were met. In the case of end-of-waste (EOW), a certain type of waste ceases to be waste. Article 6 of the Waste Directive lays down the EOW criteria. A common criterion is that waste undergoes a recovery operation, including recycling. After a recovery operation a substance or object needs to comply with specific criteria which are developed in accordance with the following four conditions. First, a substance or object is commonly used for specific purposes. The second condition brings in the need for an existing market or demand – the further use has to be fairly certain. The third condition relates to the first one – the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products. The fourth condition is that the use of the substance or object will not lead to overall adverse environmental or human health impacts. The criteria should include limit values for pollutants where necessary and should take into account any possible adverse environmental effects of the substance or object. In the introduction to the Waste Directive, in scene 22, possible categories for which EOW criteria specifications and criteria should be developed are introduced: construction and demolition waste, some ashes and slags, scrap metals, aggregates, tyres, textiles, compost, waste paper, and glass. It is also stated there that for the purposes of reaching EOW status, a recovery operation may be as simple as the checking of waste to verify that it fulfils the EOW criteria. The core of the waste and by-product legislation in the EU is illustrated in Table 1.

The Commission intends to prepare end-of-waste criteria initially for ferrous scrap, aluminium scrap, copper scrap, waste paper, and waste glass (Joint Research Centre, 2009a). The first background documents were formulated for aluminium scrap and ferrous scrap in May 2009. At the moment there is no information about end-of-waste criteria being prepared for steelmaking slags. The European Commission's Joint Research Group has prepared two important publications concerning end-of-waste criteria: End of Waste Criteria, final report (Joint Research Centre, 2008) and the Study on the selection of waste streams for End of Waste assessment, final report (Joint Research Centre, 2009b). In both publications slags from steel production are mentioned.

Before we can estimate the status of different materials used in the case study in the light of the waste legislation, two important points have to be emphasised. The industry itself uses a wide range of expressions to describe materials that are produced in industrial processes – by-products, co-products, intermediate products, non-core products, or subproducts. In Community or national environmental law, none of these expressions have any meaning, since materials are simply waste or not. Second, when drawing conclusions about the status of the materials concerned, we have to follow

the current legislation. This means that ECJ decisions and communication from the Commission to the Council and the European Parliament on the Interpretative Communication on waste and by-products play a crucial role (COM/2007/59 final). However, and fortunately for us, Articles 5 and 6 in the new Waste Directive are based on ECJ case law.

### 3.1.1. General notions on ECJ case law

The ECJ has stressed the following themes in its decisions. First, the definition of waste must be interpreted widely, since a high level of environmental protection is the leading objective of EC environmental policy, according to the previous Waste Directive (2006/12/EC), the new Waste Directive, and Article 191(2) of the Treaty of Lisbon (Treaty of Lisbon amending the Treaty on European Union and the Treaty establishing the European Community (2007/C 306/01)). The second notion takes into account the variety of materials and processes which are involved in industrial practices. Therefore, the decision as to whether a material is waste or not must be taken by the competent authority on a case-by-case basis, focusing on the factual circumstances. Third, even if a material otherwise satisfies the criteria created by ECJ case law and would therefore not be considered waste, factual circumstances could change this presumption. If a material is, in practice, discarded, it must clearly be considered and treated as waste. The importance of the notion of “discarding” is thus clear.

### 3.2. Finland

Finnish waste legislation is based on the Waste Act (1072/1993) and Waste Decree (1390/1993), which are in accordance with the EU legislation. The link between national and EU legislation is becoming increasingly strong in the field of waste management. Thus there are only a few areas of waste legislation that are not yet covered by EU legislation. As mentioned before, all member states have to implement this new Waste Directive by December 12, 2010. Therefore, the national legislation is being revised at the moment.

The Waste Act gives definitions of “waste” and “hazardous waste”. Section 3 of the Waste Act defines waste as “any substance or object which the holder discards or intends, or is required, to discard”, which is an identical definition to that in the Waste Directive. The Waste Decree specifies this definition with a list of objects and materials which are to be classified as waste. Moreover, the Ministry of the Environment has drawn up by virtue of the Waste Act a Decree (1129/2001) on the list of the most common wastes and of hazardous wastes. This list is similar to the aforementioned List of Wastes given by the European Commission (Commission Decision 2000/532/EC). The list of the most common wastes contains examples, and therefore it is not a comprehensive list, and, conversely, not all the objects or substances mentioned in it are always considered to be waste. An object or substance is considered to be waste only if it fulfils the criteria for waste laid down in Section 3(1)(1) of the Waste Act. Waste in that list is hazardous if it is marked so, unless the Centre for Economic Development, Transport and Environment decides otherwise by virtue of Section 3a (2)(1) of the Waste Decree (amendments 472/1996 and 1815/2009 to the Decree).

According to Section 1 of the Waste Act, the purpose of the Act is to support sustainable development by promoting the rational use of natural resources, and preventing and combating the hazards and harm to health and the environment arising from wastes. The principle of sustainable development should guide the environmental authorities in different aspects of their activity. The Supreme Administrative Court of Finland (in Finnish: KHO) made a reference to the principle in a precedent KHO 2005:90. In this precedent ferrochromium slag was considered a side-product (not waste). The

**Table 1**  
Waste and by-product legislation in the EU.

Term	Explanation
Waste	“Any substance or object which the holder discards or intends or is required to discard” (Waste Directive Art. 3 (1)).
By-product	A substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste but as being a by-product only if certain conditions laid down in Article 5 of the Waste Directive are met.
End-of-waste status	Certain specified waste shall cease to be waste when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with certain conditions laid down in Article 6 of the Waste Directive.
Product	Under specific product legislation.

court stated that the process in the metal-making plant was deliberately constructed in such a way that the slags could be directly handled to be exploitable by-products which were immediately, or after a short period of intermediate storage, sold, to be used, among other things, in frost insulation and road construction. The price for which the by-products were sold covered the manufacturing costs. The slags were not discarded in any phase of the process, and there was heavy demand for the by-products, which caused no harm to health or the environment. Additionally, as one of the justifications, the court mentioned that the use of the slag as a product could replace the use of fine aggregates, which promoted the rational use of natural resources and reduced the waste being generated. All the four conditions set for by-products in the Waste Directive can be found in the precedent KHO 2005:90; the by-product is used directly (without any further processing other than normal industrial practice), the by-product is produced as an integral part of a production process, and its further use is certain and lawful. Therefore it seems that the new Waste Directive will not bring significant changes to the current Finnish legal praxis concerning by-products.

In another decision by the Supreme Administrative Court of Finland, KHO 20.9.2005/2413 (not published as a precedent), nickel slag ceased to be waste. Plant A produced nickel slag in their process, which was delivered to Company B as waste. Company B dried and sieved the slag. After this drying and sieving process the nickel slag was no longer considered to be waste because the granular slag was immediately supplied as a packaged product to be used in sandblasting or as raw material in roofing felt production, without overall adverse environmental impacts when used appropriately.

Whether steelmaking slags are considered to be products or waste according to current legislation is decided in the environmental permit in each individual case. The environmental permit for the Ruukki mill in Raahe (Northern Finland Environmental Permit Authority 13/06/2; Vaasa Administrative Court 07/0242/1 and the Supreme Administrative Court KHO 20.8.2008/2022: no changes concerning waste/by-product issue) refers to the list of the most common waste and hazardous waste (1129/2001). The permit categorises some of the steelmaking slags generated in parallel with the production of steel under the codes Waste from the processing of slag (10 02 01) and Unprocessed slag (10 02 02). Some of the slags may be used as a fertiliser under the Fertiliser Act (539/2006) without needing another environmental permit. The slags may also be used as earthwork material in the plant area without an environmental permit. The Authority refers to the precedent KHO 2005:90 and states that granulated blast furnace slag and crushed aggregate made of air-cooled blast furnace slag are not waste. Similar regulations are given in the environmental permit for the Ovako Steel mill in Koverhar (Western Finland Environmental Permit Authority 30/2006/1, Vaasa Administrative Court 09/0143/1, under the appeal process in the Supreme Administrative Court). It is stated in the environmental permit for the Ovako Steel mill in Imatra (Eastern Finland environmental permit authority 126/04/2, Vaasa Administrative Court 07/0100/1 final) that the steelmaking slag generated in the steelmaking process is categorised as permanent waste unless the waste legislation and classification at each individual time lead to another classification. In conclusion, some of the slags produced in the steelmaking process are by-products, at least when their further use is for fertilisation or earthworks in the plant area.

#### 4. Case study

In our previous research we tested the ability of various different solvents to dissolve calcium selectively from steelmaking

slags so that the solution thus formed is favourable for carbonation (Eloneva et al., 2009). We found that ammonium salt solutions (ammonium chloride, ammonium nitrate, and ammonium acetate) were the most promising solvents amongst those tested. These solvents dissolved calcium efficiently and selectively. After the removal of the residual slag, carbon dioxide was introduced into these solutions and calcium carbonate precipitated. The solvents were found to be recyclable (Said et al., 2009), although some minor losses of ammonia were noted. Since the method proceeds well at low temperatures (such as room temperature) and at atmospheric pressures, it can be expected that the most energy intensive steps are crushing of the slag and mixing of the solutions in the reactors. Preliminary feasibility calculations revealed that production of power required for these steps would generate clearly less CO<sub>2</sub> than what would be fixed by the method (i.e. no more than 50 kg per ton of CO<sub>2</sub> fixed as CaCO<sub>3</sub>) (Eloneva et al., 2010). Costs related to vaporization losses of ammonia were calculated to be roughly 30–40 € per ton of CO<sub>2</sub> fixed as CaCO<sub>3</sub>, which can easily be covered by selling the produced pure calcium carbonate (price of pure precipitated CaCO<sub>3</sub> ≥100 € per ton (Roskill, 2008)) with additional benefit coming from the selling of the CO<sub>2</sub> emission allowances (~13 € per ton (Point Carbon, 2009)). In addition, ongoing research indicates that losses of evaporating ammonia are clearly smaller than the amount used in the feasibility calculations (Mannisto, 2010). Equipments required for the method to be used in industrial practise should not differ significantly from the conventional process equipments, such as those used in manufacture of pure precipitated calcium carbonate. Therefore, the method's investment and operational costs should be tolerable. However, the viability of the carbonation method based on steelmaking slags and ammonium salt solutions is partly dependent on the quality of the residual slag (Fig. 1). It is desirable to produce a residue that is not environmentally harmful. Therefore the effects of the method on the characteristics of the steel converter slag from Ruukki's Raahe Works, in particular on the leaching behaviour of the harmful elements, were investigated experimentally.

Batches of 100 g of steel converter slag (<500 μm) were dissolved in 11 aqueous solutions of ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), or ammonium chloride (NH<sub>4</sub>Cl) (2 M). The solutions were stirred at 500 rpm at room temperature and under atmospheric pressure (Fig. 2). After 2 h, the residual slags were removed from the solutions by filtration and washed. The residual slags were then dried at 120 °C overnight. This was repeated 4–5 times to ensure there was enough material for the leaching tests (SFS-EN 12457-3), as well as for X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF) analyses. The steel converter slag fraction used was also analysed by XRD and XRF. These experimental conditions were selected on the basis of previous results (Eloneva et al., 2009, 2010), which indicated that the grain size of the steel converter slag should not

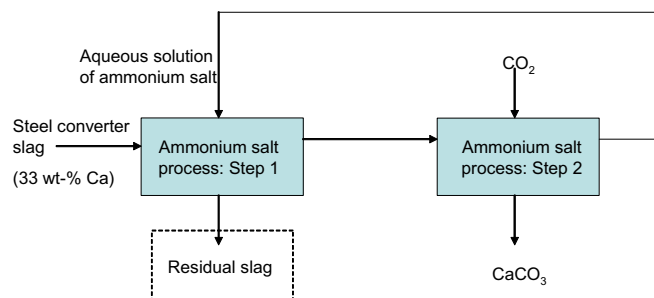


Fig. 1. Simplified process scheme of carbonation method based on steelmaking slags and ammonium salt solutions.

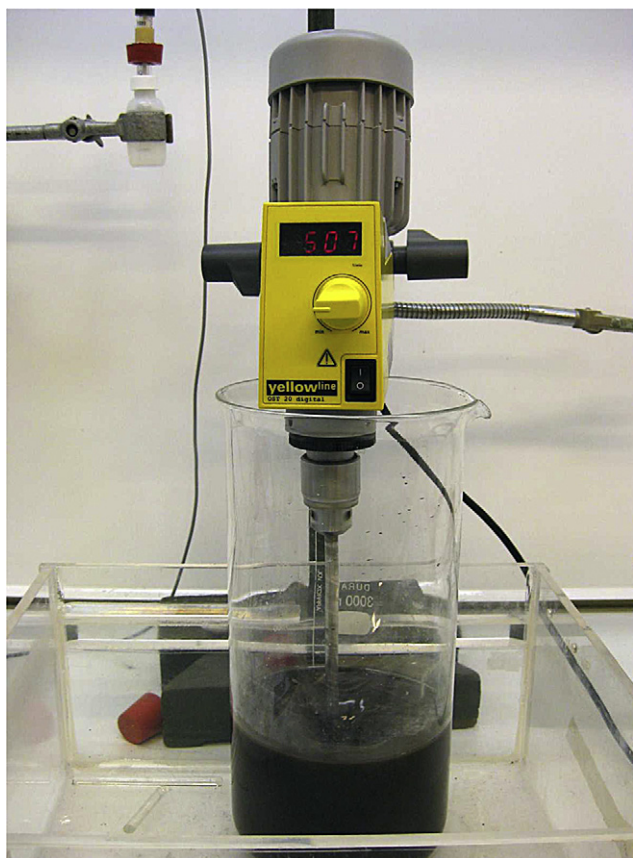


Fig. 2. Photo of the test facility used for preparing the residual slags.

be increased to above 500  $\mu\text{m}$  and solid to liquid ratios over 100 g/l (in 2 M solution) should be avoided.

According to the XRD analysis (Table 2), the steel converter slag was composed of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), wuestite ( $\text{FeO}$ ), calcium oxide ( $\text{CaO}$ ), larnite ( $\text{Ca}_2\text{SiO}_4$ ), srebrodolskite ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ), and iron ( $\text{Fe}$ ). The residual slags after extraction with the solvents contained the same phases as the steel converter slag, except those of  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$ , indicating that these had completely dissolved. While quite complete dissolution of larnite could have been expected, as a synthetic larnite dissolves readily in water (Santos et al., 2009), it might have been that the inert layer of for example  $\text{SiO}_2$  was deposited on the reactive surface as calcium dissolved from its silicate preventing some of the calcium from dissolving as explained by Kodama et al. (2008). Alternatively, the calcium silicate phase might have been present as inclusion within the undissolving phases preventing contact of the phase with the solvent as explained by Doucet (2010).

The calcium contents of the residual slags were significantly smaller than that of the original steel converter slag, while the contents of the other major elements of the slag ( $\text{Fe}$ ,  $\text{Si}$ ,  $\text{Mn}$ ,  $\text{Mg}$ , and

$\text{V}$ ) had increased (Table 3). This was expected, as these solvents had earlier proved to be quite selective for calcium, while, at the same time, the mass of the slag had decreased by  $\sim 25$  wt-% in all the solvents. According to the results from the XRF analyses, approximately 40% of the slag's calcium had dissolved. This is in quite a good agreement with the previous results (Eloneva et al., 2010), where  $\sim 45\%$  of the slag's calcium was dissolved under very similar conditions, although the grain size of the slag was slightly smaller (125–250  $\mu\text{m}$  instead of  $\leq 500$   $\mu\text{m}$ ) and reaction time shorter (1 h instead of two). Based on the previous experiments, lower solid to liquid ratio would have resulted with slightly higher calcium extraction ratio ( $\sim 10\%$ -units).

The results of the leaching tests are listed in Table 4, together with the solubility data of the steel converter slag. The solubility of most of the elements in the residuals is less than or similar to that of steel converter slag. On the other hand, the solubility of chromium ( $\text{Cr}$ ) and  $\text{V}$  is significantly higher from the residual slags than from the steel converter slag. Furthermore, the solubility of molybdenum ( $\text{Mo}$ ), chlorine ( $\text{Cl}$ ), and sulphate ( $\text{SO}_4$ ) is higher from the residual slag of the experiments with the  $\text{NH}_4\text{Cl}$  solution than from the steel converter slag. The solubility of nitrate ( $\text{NO}_3$ ) from the residual slag of the experiments with the  $\text{NH}_4\text{NO}_3$  solution is much higher than its solubility from the residual slag of the experiments with  $\text{NH}_4\text{Cl}$  or  $\text{CH}_3\text{COONH}_4$ , indicating that part of the  $\text{NH}_4\text{NO}_3$  solvent's anions ( $\text{NO}_3^-$ ) combine with the slag during the extraction.

## 5. Adapting the legislation to our case

According to the environmental permit in question, Ruukki's steel converter slag is a by-product that falls under the Fertiliser Act (539/2006) (Northern Finland Environmental Permit Authority 13/06/2; Vaasa Administrative Court 07/0242/1 and the Supreme Administrative Court KHO 20.8.2008/2022). Section 5 of the Act states that a fertiliser must not contain such an amount of harmful substances, products, or organisms that the fertilisers used in accordance with its instructions may cause harm to human or animal health or safety or plant health, or the environment. Annex IV to the Decree on Fertilisers of the Ministry of Agriculture and Forestry concerning the Fertiliser Act (12/07) deals with harmful substances, products, or organisms in fertilisers. There are limits set for harmful metals ( $\text{As}$ ,  $\text{Hg}$ ,  $\text{Cd}$ ,  $\text{Cr}$ ,  $\text{Cu}$ ,  $\text{Pb}$ ,  $\text{Ni}$  and  $\text{Zn}$ ) and their maximum concentration in fertilisers. The Decree does not contain leaching limits for the slag, but it is mentioned in Annex I that the solubilities of the by-products used as liming materials should be below those set for conventional waste materials in the Government Decision on Landfills (861/1997, amendment 202/2006). For the elements mentioned there (Table 5), the solubilities of the elements of the residual slags are all below those limits. Nevertheless, this Government Decision does not give leaching limits, for instance, for  $\text{V}$ . The residual slag may be found to endanger human or animal health or safety or plant health, or the environment because of the leaching of  $\text{V}$ . Therefore the residual slag might not be accepted as a fertiliser. Additionally, when the suitability of the residual slag as liming material is considered, the main criteria are the properties required for the product (such as neutralizing capacity). The absence of the free calcium oxide and

Table 2  
Phases in steel converter slag and in the residual slags identified by XRD analysis.

Material	Phases identified
Steel converter slag	Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), wuestite ( $\text{FeO}$ ), calcium oxide ( $\text{CaO}$ ), larnite ( $\text{Ca}_2\text{SiO}_4$ ), srebrodolskite ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ), iron ( $\text{Fe}$ )
Residual slag from $\text{CH}_3\text{COONH}_4$ solution	Larnite ( $\text{Ca}_2\text{SiO}_4$ ), wuestite ( $\text{FeO}$ ), iron ( $\text{Fe}$ ), srebrodolskite ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ )
Residual slag from $\text{NH}_4\text{NO}_3$ solution	Larnite ( $\text{Ca}_2\text{SiO}_4$ ), srebrodolskite ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ), wuestite ( $\text{FeO}$ ), iron ( $\text{Fe}$ )
Residual slag from $\text{NH}_4\text{Cl}$ solution	Wuestite ( $\text{FeO}$ ), srebrodolskite ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ), iron ( $\text{Fe}$ ), larnite ( $\text{Ca}_2\text{SiO}_4$ )

Table 3  
Composition of the steel converter slag and residual slags as determined by XRF analysis (wt-%, only elements present at  $\geq 1$  wt-% are shown).

Material	Ca	Fe	Si	Mn	Mg	V
Steel converter slag	32.5	15.5	5.7	2.5	1.0	1.35
Residual slag from $\text{CH}_3\text{COONH}_4$ solution	25.4	21.9	7.6	3.4	1.3	1.87
Residual slag from $\text{NH}_4\text{NO}_3$ solution	25.9	21.7	7.8	3.5	1.3	1.90
Residual slag from $\text{NH}_4\text{Cl}$ solution	24.9	20.8	7.5	3.3	1.3	1.82

**Table 4**  
Solubility of the residual slags based on the shaking test (SFS-EN 12457-3) and solubility of the steel converter slag (Ruukki, 2009) (mg/kg).

Element	Steel converter slag	Residual slag from		
		CH <sub>3</sub> COONH <sub>4</sub> solution	NH <sub>4</sub> NO <sub>3</sub> solution	NH <sub>4</sub> Cl solution
As	0.1–0.2	<0.006	<0.006	<0.006
Ba	2–7	0.03	0.01	0.02
Cd	0.01–0.02	<0.003	<0.003	<0.003
Cr	0.06–0.1	0.81	1.1	0.93
Cu	0.01–0.2	<0.01	<0.01	<0.01
Hg	0.001–0.003	0.001	<0.001	0.001
Mo	0.05–0.08	0.06	0.07	0.10
Ni	0.05	0.01	<0.01	<0.01
Pb	0.01–0.2	<0.01	<0.01	<0.01
Sb	0.01–0.2	<0.01	<0.01	<0.01
Se	0.05–0.1	<0.05	<0.05	<0.05
V	0.06–0.2	190	170	150
Zn	0.06–1.2	<0.01	<0.01	<0.01
Co	0.01–0.03	<0.03	<0.03	<0.03
F	1–12	<0.1	3.5	<0.1
Cl	8–20	4.6	4.9	340
SO <sub>4</sub>	20–120	81	110	140
Br	Not available	<0.1	<0.1	<0.1
NO <sub>2</sub>	Not available	<0.1	2.9	<0.1
NO <sub>3</sub>	Not available	3.5	510	<0.1
PO <sub>4</sub>	Not available	<0.1	<0.1	<0.1
Sn	Not available	<0.01	<0.01	<0.01

lower calcium content strongly suggest that residual slag does not have suitable neutralizing capacity, which is dependent on reactive lime, thus it would probably make residual slag unsuitable for such a use. While there is not yet utilisation option for the residual slag, it could be prevented from being a waste by inventing one.

Currently, there are no actual leaching limits for residual slag. However, there are leaching limits for different waste materials on landfills (Table 5) (Government Decision on Landfills (861/1997, amendment 202/2006)) and at this moment those are the only existing legal leaching limits that the results can be compared to. The leaching limit of Cr for permanent waste materials is only 0.5 mg/kg, and thus the leaching of Cr from the residual slag would prevent it from being suitable for a permanent waste landfill site. The leaching of Cr would, however, be below the leaching limit set for hazardous waste material, as well as those set for the conventional waste material mentioned above. Therefore, if no other utilisation option for the residual slag will be found, it would probably be handled as waste.

**Table 5**  
Leaching limits for different waste materials on landfills (mg/kg) (Government Decision on Landfills (861/1997, amendment 202/2006)).

Element	Permanent waste	Conventional waste	Hazardous waste
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	5
Cr	0.5	10	70
Cu	2	50	100
Hg	0.01	0.2	2
Mo	0.5	10	30
Ni	0.4	10	40
Pb	0.5	10	50
Sb	0.06	0.7	5
Se	0.1	0.5	7
Zn	4	50	200
F	10	150	500
Cl	800	15 000	25 000
SO <sub>4</sub>	1000	20 000	50 000
Phenol index	1	–	–
DOC	500	800	1000
TDS	4000	60 000	100 000

## 6. Conclusions

The CO<sub>2</sub> mineralisation method, based on steelmaking slags and ammonium salt solutions, was found to change the slag's quality. Experimental work revealed that the CaO and Ca(OH)<sub>2</sub> phases were completely dissolved from the steel converter slag during the dissolution step of the method. Additionally, the calcium content of the residual slag was significantly less than that of the steel converter slag used in the experiments. In total, the mass of the slag decreased by 25 wt-%. While the solubility of most of the elements that were tested had decreased, the solubility of the V and Cr had clearly increased. The selection of an ammonium salt solution (from among ammonium chloride, ammonium nitrate, and ammonium acetate) seemed to have an effect only on the solubility of a few elements. Because of these changes in the quality of the slag, the residual slag would probably not fulfil the property requirements set for steel converter slag used as a liming material. However, residual slag would probably be handled as waste, unless another suitable utilisation option was invented for it. While it is hoped that this will not prevent slag from being used as a raw material for CO<sub>2</sub> mineralisation, attention should be paid to the increased solubility of V and Cr. Further, the oxidation degree of Cr in the residual slag should be investigated, as Cr(VI) is considered toxic, while Cr(III) is a necessary trace element for mammals (Reijonen, 2009). As a result, a treatment method may have to be found for the residual slag. Furthermore, it is recommended that the leaching limit of vanadium should be studied and set, in order to improve the current standard of the leaching limits (Table 5).

The European Union has adopted a new Waste Directive, which should clarify the definition of waste. Currently, the steel converter slag used in this case study is defined as a by-product (not waste) and it is likely to continue to be a by-product according to the upcoming waste legislation. However, if it is used for CO<sub>2</sub> mineralisation instead of liming, its legal status will be evaluated again. While its use as a raw material for CO<sub>2</sub> mineralisation should quite easily fulfil the third and fourth conditions of Article 5 of the Waste Directive, i.e. its use would be lawful and certain, and it would be produced as an integral part of the production process (condition 2), there is a need for further processing and thus condition 1 would not be met. On the other hand, the CO<sub>2</sub> mineralisation process could possibly be seen as an end-of-waste procedure.

Besides the issue of the residual slag there are a few other issues that have to be considered before the method is suitable for industrial use. While previous research (Eloneva et al., 2009) indicates that the CaCO<sub>3</sub> end product of the method is of high quality, its suitability as a paper filler or in other valuable use has to be investigated in practice. As a result of varying properties of the different steelmaking slags, the method is not necessarily suitable for just any slag, therefore the suitability of the each slag type as raw material for the method has to be investigated separately. In case the steel plant and the paper mill (the end product user) are situated very close to each other, they will form an industrial ecosystem in which waste and by-products (CO<sub>2</sub> and steelmaking slag) are effectively utilized as raw materials by co-located industry to create environmental and economic synergies (see e.g. Korhonen et al., 2004). If the operation place of the method is not situated close to both, steel plant and paper mill, then either raw material (steelmaking slag) or end product (CaCO<sub>3</sub>) has to be transported. Since transportation is a significant source of CO<sub>2</sub>, a maximum allowable distance between the steel mill and end product user for this method to have negative CO<sub>2</sub> emissions must be considered. In addition, environmental effects of the method's CaCO<sub>3</sub> end product should be analysed from its entire life cycle. Since this would be quite extensive it deserves a separate paper.

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