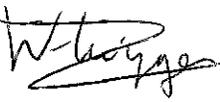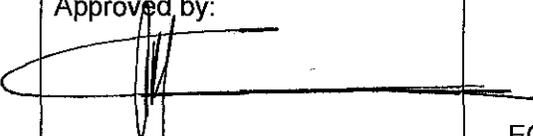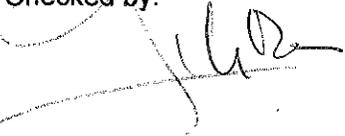# Mineral CO$_2$ sequestration by carbonation of industrial residues
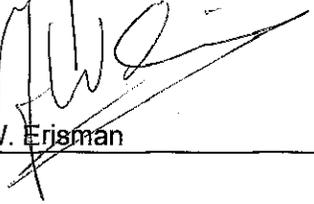
Literature overview and selection of residue

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Preface

Abstract

The carbonation of industrial residues can be used to reduce CO_2 emissions by CO_2 sequestration. In this report a selection of suitable residues is made. A first selection step is made on the basis of a set of required residue properties. A literature overview on properties of selected residues and on carbonation experiments reported with these residues is given. The chemistry during carbonation is discussed and the effect of carbonation on the leaching properties of the materials is studied. Finally, the carbon dioxide sequestration potential of selected residues is calculated and residues are selected for carbonation experiments.

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1. Introduction

In a literature review on CO_2 sequestration by mineral carbonation (Huijgen & Comans, 2003), we have introduced the use of solid residues as an alternative feedstock for mineral carbon dioxide sequestration. Main advantages of the use of residues instead of ores are their availability at low costs near energy and industrial sites (Huijgen & Comans, 2003; Fauth *et al.*, 2002). The principles behind mineral CO_2 sequestration are similar for both ore and residue carbonation. In fact, the major elements of *e.g.* MSWI bottom ash (Si, Ca, Al and Fe) are present in a comparable concentration as in igneous rocks (Johnson *et al.*, 1995). However, trace metals and soluble salt concentrations are typically enriched by several orders of magnitude compared to the average composition of the earth's crust. Although only few studies of carbon dioxide sequestration in solid residues have been published, many studies have been performed on the natural ageing of solid residues and the consequences of carbonation for the leaching properties of these materials. These studies are discussed in this report.

The aims of this report are:
- Give an overview of literature on carbonation of residues and the effect of carbonation on leaching[1].
- Select suitable residues for potential mineral CO_2 sequestration in the Netherlands.

For more information on mineral CO_2 sequestration in general, we refer to the previously published literature reviews (Huijgen & Comans, 2003 & 2005a)(Huijgen & Comans, 2005).

In Chapter 2 the requirements for residues potentially suitable for mineral CO_2 sequestration are discussed and a classification of solid residues is given, so that a first selection of a residue for mineral CO_2 sequestration can be made. Chapter 3 deals with the overview of literature on the carbonation of residues. Subjects of discussion are the properties of the residues, the chemical changes occurring during carbonation, experimental carbonation studies reported and the influence of carbonation on the leaching properties of the materials. Finally, in Chapter 4 the CO_2 sequestration capacity of various residues is quantified and residues are selected for further study on mineral CO_2 sequestration.

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[1] The number of studies on these subjects is large. Therefore, this study cannot discuss all the existing literature. A selection of papers has been made according to their relevance with regard to carbon dioxide sequestration properties. For more detail the reader is referred to the original literature.

2.   First selection of residues

Because of the large number and variety of industrial residues, a first selection of potentially suitable residues for mineral carbon dioxide sequestration is made based on the following requirements:

- *The residue is solid.*
  Use of e.g. liquid residue streams might be possible[2], but controlled storage of the carbonated product is more difficult than for solid materials. Therefore, liquids are left out of consideration.
- *The residue is of inorganic nature*
- *The residue is alkaline (pH>8)*
  In order to be able to react with acid CO_2 the residue must be sufficiently alkaline.
- *The residue contains non-carbonated calcium and/or magnesium minerals in an available (i.e. for reaction with CO_2) form.*
  In a previous study, it has been shown that it is preferable to carbonate these elements compared to e.g. alkali metals, Ba, Sr or Fe, since these are major elements able to form stable carbonates (Huijgen & Comans, 2003).
- *The residue has to be produced (or otherwise available) in the Netherlands.*
  The selection of residues is limited to the Dutch context.[3]

On the basis of these selection criteria, residue types have been selected (Table 2.1). In general the selected materials are by-products of (combustion) processes at high temperatures or construction residues. For each group of residues, some examples of alkaline solid residues are given.

Table 2.1   *Examples of selected alkaline solid residues*

Residue group	Example
Ash	MSWI[4] bottom ash
Slag	Coal slag
	Steel (LD)[5]-slag
	Blast furnace slag
Fly ash	Coal fly ash
	MSWI fly ash
Air pollution control (APC) residue	MSWI APC residue
Construction and demolition waste	Cement
	Concrete
	Asbestos[6]

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[2] An example is the carbonation of aqueous residue streams for the remediation of heavy metal containing residue water (Enick *et al.*, 2001).

[3] For example, oil shale is not taken into account although the amount of oil shale produced worldwide is very large. For example, the reported residue production of one particular USA industry is 675 kton/y (Essington, 1991). However, in the Netherlands oil shale residue is not available.

[4] Municipal solid waste incinerator.

[5] Linz Donawitz steel process.

[6] The bulk of asbestos consists of chrysotile (Goff & Lackner, 1998). This mineral is a member of the serpentinite group and is highly capable of binding CO_2. Residue chrysotile asbestos could be used as feedstock material for carbon dioxide sequestration if it is relatively uncontaminated by other materials.

Among these residues, a further selection will be made in Chapter 4 on the basis of the following two main criteria:

- *The residue has a high CO_2 sequestration capacity per unit of mass.*
  A high specific CO_2 sequestration capacity reduces the amount of material that has to be processed to sequester a certain amount of carbon dioxide.
- *The residue has a high total CO_2 sequestration capacity in the Netherlands.*
  A high total CO_2 sequestration capacity enables a larger contribution to the reduction of CO_2 emissions. In addition, given the variable composition of residues, the optimal process conditions for the various residues do probably also differ. For reasons of 'economy of scale', it is preferable to develop carbon sequestration routes for residues that are available in sufficiently large amounts.

In addition to the requirements discussed above, the following properties are desirable, *e.g.*:

- *The residue is available near the carbon dioxide source.*
  Thus transport is minimised and costs are reduced.
- *The carbonated product can be utilized beneficially, e.g. in construction.*
  Beneficial re-use improves the economics of the process and reduces its environmental impact. Furthermore, public acceptance of mineral CO_2 sequestration is likely to be higher if a useful and environmentally friendly application of the formed products is available.
- *The leaching of potentially harmful elements from the residue decreases due to carbonation.*
  This possible side effect can have positive environmental impacts and is discussed further in Section 3.3.

In the next chapters, first the literature on carbonation of the residues such as those presented in Table 2.1 will be discussed briefly. Finally, residues will be selected on the basis of the above criteria.

# 3. Carbonation of residues: literature overview

3.1 Chemistry

In many studies the composition and mineralogy of solid residues before and after weathering have been studied. As an example, the elemental composition of some residues is given in Appendix A. In addition, the pH of a saturated solution and the acid neutralising capacity are given. These properties are meant to be indicative, since only a limited number of studied has been included and the composition of these residues may vary significantly. As an example, a number of mineralogy studies are given below.

Table 3.1   *Example studies on the mineralogy of alkaline solid residues*

Residue	Unweathered	Weathered
MSWI bottom ash	(Kirby & Rimstidt, 1993) (Tedjar, 1999) (Freyssinet *et al.*, 2002) (Zevenbergen, 1994)	(Tedjar, 1999) (Zevenbergen, 1994) (Piantone *et al.*, 2004)
MSWI electrostatic precipitator ash	(Eighmy *et al.*, 1995)	
Coal fly ash	(Reddy *et al.*, 1994) (Schramke, 1992) (Warren & Dudas, 1985) (Sarbak & Kramer-Wachowiak, 2001)	(Reddy *et al.*, 1994) (Schramke, 1992) (Warren & Dudas, 1985)
Coal combustion FBC[7] ash	(Fauth *et al.*, 2002)	(Fauth *et al.*, 2002)
Coal combustion FGD[8] ash	(Fauth *et al.*, 2002)	(Fauth *et al.*, 2002)
Steel slag	(Yan *et al.*, 2000) (Johnson *et al.*, 2003)	(Johnson *et al.*, 2003) (Huijgen *et al.*, 2004)
Oil shale solid residue	(Essington, 1991) (Reddy *et al.*, 1991) (Reddy *et al.*, 1994)	(Essington, 1991) (Reddy *et al.*, 1991) (Reddy *et al.*, 1994)
Coal APC residues	(Tawfic *et al.*, 1995)	(Tawfic *et al.*, 1995)

Residues are generally rich in calcium in which case Ca-minerals often control the pH (*e.g.*, Meima, 1997). The carbonation of Ca-minerals is the main CO_2 sequestration reaction for residues. Different reactions can be distinguished:
1. Residues with a high native pH value (>10) often contain portlandite, which controls the solubility of Ca as well as pH. Portlandite is carbonated relatively easily (Huijgen *et al.*, 2003) according to:

$$Ca(OH)_2 \text{ (s)} + CO_2 \text{ (g)} \rightarrow CaCO_3 \text{ (s)} + H_2O \text{ (l)} \qquad \text{(eq. 1)}$$
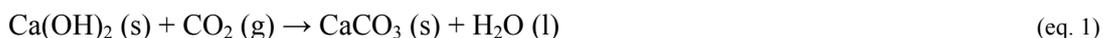
This reaction has been reported in *e.g.* MSWI-bottom ash (Meima & Comans, 1997) and cement (Shafique *et al.*, 1998).

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[7] Fluid Bed Combustion
[8] Flue Gas Desulphurisation

2. Another group of Ca-minerals that is often present in residues are Ca-silicates, such as $CaSiO_3$ (wollastonite). The carbonation reaction can either be written in terms of naturally occurring minerals:
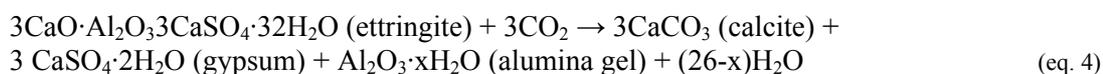
$$CaSiO_3 + CO_2 \rightarrow CaCO_3 \text{ (s)} + SiO_2 \qquad \text{(eq. 2)}$$

Or, more generally, the carbonation of Ca-silicates can be represented as:
$CaO \cdot nSiO_2 \cdot mH_2O$ or C-S-H (s) $+ CO_2$ (g)
$\rightarrow CaCO_3$ (s) $+ nSiO_2$ (s) $+ mH_2O$ $\qquad \text{(eq. 3)}$

Such processes have been reported for the carbonation of *e.g.* cement (Lange *et al.*, 1996) and steel slag (Huijgen *et al.*, 2005b).

3. Finally, a Ca-mineral present in many residues is ettringite. The carbonation of ettringite can be written as:

$3CaO \cdot Al_2O_3 3CaSO_4 \cdot 32H_2O$ (ettringite) $+ 3CO_2 \rightarrow 3CaCO_3$ (calcite) $+$
$3\ CaSO_4 \cdot 2H_2O$ (gypsum) $+ Al_2O_3 \cdot xH_2O$ (alumina gel) $+ (26-x)H_2O$ $\qquad \text{(eq. 4)}$

Ettringite is carbonated easily and is not stable at even slightly lowered pH-values. Therefore, ettringite is usually absent in carbonated residues. This carbonation reaction has been reported for, among others, cement (Lange *et al.*, 1996). Essington concluded that the dissolution of ettringite and the subsequent precipitation of calcite dominate the weathering of oil shale residue resulting in a pH drop to 9.0 after carbonation (Essington, 1991).

Studies on the carbonation of calcium phases showed that the carbonation process might be influenced by the presence of other ions. For example, Schramke has reported that the rate at which coal fly ash is neutralised by carbon dioxide is directly proportional to the sulphur concentration of the material (Schramke, 1992). SO_4^{2-} has a direct effect on the calcite formation rate due to the precipitation of gypsum ($CaSO_4$). Mg^{2+} was reported to inhibit the precipitation of calcite and lead to the formation of aragonite instead of calcite (Schramke, 1992).

Magnesium, generally being present in smaller amounts than calcium in residues, can also be carbonated and, therefore, used to sequester CO_2 as has been reported during weathering of *e.g.* oil shale residue (Reddy *et al.*, 1991). For example:

$$Mg_2SiO_4 \text{ (fosterite)} + 2CO_2 \text{ (g)} \rightarrow 2MgCO_3 \text{ (s)} + SiO_2 \text{ (s)} \qquad \text{(eq. 5)}$$
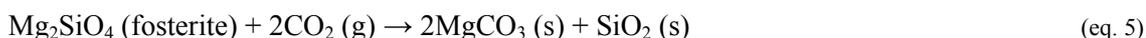
A few extra remarks on the carbonation of residues as compared to ores have to be made here:
- In general the carbonation of solid residues is faster than for ores, for three major reasons. First, calcium is generally the predominant alkaline component in residues and calcium is known to be carbonated more rapidly than magnesium (Huijgen *et al.*, 2003), which often dominates in ores particularly suitable for mineral CO_2 sequestration, such as olivine (Mg_2SiO_4). Second, residues tend to have a relatively open structure and greater reactive surface area. Finally, residues such as slags and ashes that are formed at high temperatures and subsequently rapidly cooled, are geochemically instable and, therefore, reactive.
- Due to the heterogeneous composition of residues, theoretically, various (bi)carbonates might be formed. In addition to the solid carbonate minerals of the alkaline earth metals, also other more soluble (bi)carbonates might be formed. Furthermore, at the high pressure typically applied during the carbonation process, (bi)carbonates could potentially be formed that are unstable at atmospheric conditions. These (bi)carbonates might therefore (slowly) loose their bound carbon dioxide from the carbonated product. Both effects have to taken into account when experimentally measuring the carbonation rate of residues and assessing the environmental impacts of storing carbonated residues. In ores such trace elements are

generally present in much lower amounts, which reduces the occurrence of these side reactions.

3.2   Carbonation experiments

Various carbonation experiments have been reported for residues. A summary of process conditions and CO_2 uptake reported is given for some carbonation experiments in Appendix B. Two groups of experiments can be distinguished. First, experiments at low pressures, typically conducted by bubbling CO_2 through an aqueous residue containing slurry or a moisturised heap of residue. Second, experiments at elevated pressure conducted in an autoclave reactor. In the first type of experiments often only the free lime and other easily dissolvable Ca-phases, such as ettringite, are carbonated and the reaction times are long. In high-pressure experiments also more tightly bound calcium, such as certain calcium silicates, can be carbonated, thus increasing the CO_2 sequestration capacity.

Various process routes have been developed for mineral CO_2 sequestration. These routes have been discussed in two literature reviews (Huijgen & Comans, 2003 & 2005a). Most process routes have been developed for the carbonation of primary minerals, but can, in principle, also be applied to mineral CO_2 sequestration by the carbonation of residues. However, as discussed in the first literature review (Huijgen & Comans, 2003), so-called direct methods (*i.e.*, one step carbonation processes) are preferable for residues. Indirect (*i.e.*, multiple step carbonation processes which often include the recycling of an extraction agent) are less suitable for residues, among others, since the inhomogeneity of residues may cause large solvent losses due to side reactions. The direct aqueous carbonation process (i.e., direct carbonation of a mineral in a slurry at elevated temperature and pressure) has been selected for carbonation experiments with both ores and residues at the Energy research Centre of the Netherlands (ECN) (see Huijgen & Comans, 2003).

In direct aqueous ore carbonation processes often salts (e.g., NaCl, $NaHCO_3$) are added to increase the carbonation rate (O'Connor, 2005). The possible need for such additional chemicals might be less or even absent if residues are carbonated instead of ores. For example, MSWI bottom ash contains considerable amounts of soluble salts by itself and additional salts may not be required. The experimental results presented in Appendix B have been either obtained by carbonation at low temperature and pressure in the presence of moisture or by the direct aqueous carbonation process.

3.3   Leaching

Leaching is an important aspect with regard to the possible beneficial utilisation of the carbonation products. Carbonation is known to be able to influence the leaching of contaminants from residues by *e.g.* precipitation of (carbonate) minerals and pH neutralisation. In addition to chemical effects, leaching may *e.g.* be increased if the matrix is ground before carbonation due to the higher reactive surface. The influence on leaching might depend on the process conditions and carbonation degree. Examples of reported influences of carbonation on the leaching properties of residues is given in Table 3.2.

Table 3.2   *Examples of reported influences of carbonation on leaching*

Residue	Leaching increased	Leaching decreased	Source
MSWI bottom ash		Zn, Pb, Ni, Cu	(Devoldere *et al.*, 2000)
	Sb	Cu, Mo, Pb, Al	(Steketee & Urlings, 1994; Steketee & Urlings, 1999)
		Cu, Mo	(Meima *et al.*, 2002)
	Cr	Cu, Ba	(Gerven van *et al.*, 2005)

	Cd	Pb, Zn	(Ecke, 2003)
		Pb, Cu	(Chimenos et al., 2003)
MSWI APC residues		Pb	(Reddy, 2000)
Steel slag	V, Si	Ba, Ca, Sr, Cl, S, Zn	(Huijgen et al., 2004)
Coal fly ash		Mn	(Reddy, 2000)
		Cd, Pb, Zn, Mn, Ni, Cu, Se	(Reddy et al., 1994)
Coal power plant APC residues		Cd, Pb, Cr, As, Se	(Tawfic et al., 1995)
Oil shale residue		F, Mo	(Reddy et al., 1991)

Two important mechanisms that occur during carbonation and reduce the leachability of elements are pH reduction and mineral neoformation. Lead and zinc in MSWI bottom ash, for example, are reported to be trapped in newly formed carbonates (Freyssinet et al., 2002). Reduction of the pH to about 8-9 results in a solubility minimum of many metal oxides (Comans et al., 1993). Another "mechanism" by which leaching can be reduced is washing. If the carbonation process is performed in an aqueous environment, washing occurs during the carbonation process. Thus, particularly mobile elements such as Cl are washed out.

A potentially important aspect in the feasibility of a residue carbonation process is the destination of the carbonated product. The physical structure of a residue may also be altered by carbonation, which could have an effect on both the leaching characteristics and the mechanical properties of the residue. For cement Lange et al. have found an increased strength after carbonation (Lange et al., 1997). Hartmann et al. have reported increased strength and reduced permeability after carbonation of a cemented radioactive residue (Hartmann et al., 1999). For concrete, however, carbonation may have a deleterious effect on its structure. The quality as a building material declines (Lange et al., 1996). Teramura et al. investigated the possibilities to carbonate waste concrete to produce a new building material. They concluded that the recycled material is useable for certain specific applications (Teramura et al., 2000). Steel slag, which has been treated with carbon dioxide and water at high temperatures, might be re-used as, for example, paving materials and building materials (Nakagawa et al., 2000). Finally, it should be kept in mind that non-carbonated residues are already often usefully applied in the Netherlands. Preferably, these beneficial re-use options should be maintained after carbonation.

3.4 Industrial processes and costs

At this stage of development of mineral carbon dioxide sequestration processes only very few industrial carbonation processes have been designed for industrial residues aimed at CO_2 sequestration. For example, Fujii et al. proposed an artificial weathering process of concrete residue for carbon dioxide sequestration (Fujii et al., 2001), based on the mineral acetic acid route of Kakizawa et al. (Kakizawa et al., 2001). In this process the calcium is first extracted from the matrix with acetic acid and then carbonated. The acetic acid is assumed to be fully recovered. An energy consumption of 13.9 MW was calculated for the sequestration of the carbon dioxide of a 100 MW 40% efficient oil-powered thermal power plant. The efficiency including CO_2 sequestration is 34.4%. The costs for CO_2 sequestration are about 35 €/ton CO_2[9], considerably lower than the costs for carbon dioxide sequestration based on wollastonite carbonation using the same process route (57 €/ton CO_2) (Kakizawa et al., 2001).

A similar process study was performed for waste cement carbonation by Iizuka et al. (2004). In this process, water was used as extraction agent instead of acetic acid. The calculated energy consumption is 25.9 MW for 100 MW of power generation and the costs associated with this energy consumption 22.6 €/ton CO_2.

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[9] In the report all costs are given in €. As exchange rate, 1\$=1€ is used.

Both carbonation processes are carried out at elevated temperature and pressure in a sequestration plant with dedicated relatively expensive process equipment. A cheaper alternative could be the low temperature and pressure approaches, such as carbonation by spraying water on heaps of e.g. steel slag or waste concrete. The carbon dioxide originates from (enforced) contact with air. Estimated costs are 8 €/ton CO_2 (Stolaroff, 2005). However, the amount of CO_2 sequestered is obviously significantly lower than in the first two processes. Reported costs are therefore not directly comparable.

4. Final selection of residues

4.1 Sequestration potential

Among the residues selected in the first selection step (see section 2), a further selection is made on the basis of their potential carbon dioxide sequestration capacity. First, the specific sequestration capacity per kilo of residue has been determined. There are two possible routes to determine this value[10]. The first option is to use the acid neutralising capacity (ANC) of the material. Based on the amount of acid required to reach a given pH[11], the CO_2 consumption can be calculated. However, the number of protons released as CO_2 dissolves differs over the pH range[12]. Furthermore, no carbonate minerals are actually formed during the ANC measurement. The sequestration capacity estimated on the basis of ANC values should therefore be considered as a lower limit. The results based on the ANC value are given in Table C.1. The second method starts with the total elementary composition. It is assumed that all calcium and magnesium can be liberated from the matrix and, subsequently, carbonated. Thus, a maximum sequestration capacity is obtained. The calculated values are given in Table C.2.

With the results given in Appendix C and the annual production of the residues in the Netherlands, the total carbon dioxide sequestration potential has been calculated for a number of selected residues, as shown in Table 4.1.

Table 4.1   *Carbon dioxide sequestration potential*[13]

Residue	Amount [kton/y][14]	Acid Neutralising Capacity		Total composition	
		CO_2 [g/kg]	CO_2 [kt/y]	CO_2 [g/kg]	CO_2 [kt/y]
MSWI bottom ash	1009	11 – 22	11.1 – 22.4	108 – 161	109.3 – 162.5
MSWI fly ash	83	55	4.6	155	12.9
CD-waste[15]	962	73	69.8	486 – 509	467.6
LD-slag	500[16]	172	86.0	325 – 407	162.5 – 203.5

The following conclusions can be drawn from the estimated potential carbon dioxide sequestration capacity of the selected residues shown in Table 4.1. The residues with the highest specific sequestration potential based on total composition are cement and steel slag. The residues with the largest sequestration potential in the Netherlands are C&D-waste, steel slag and MSWI bottom ash.

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[10] A third option sometimes applied in literature might be a calculation based on the pH-value of the residue. Although the amount of CO_2 absorbed is found to be proportional to the pH of non-weathered fly ash (Schramke, 1992) the absolute amount cannot be determined in this way because the buffer capacity of the material is overlooked.

[11] In the standard ANC test, a ground residue (<125 μm) is kept at pH 7 for three hours and then pH 4 for another three hours.

[12] At high pH-values, 1 mol eq H^+ corresponds with 0.5 mol CO_2, because 2 H^+ are created as CO_3^{2-} is formed. At medium pH-values, HCO_3^- is formed and only 1 mol H^+ is created for every CO_2 dissolved. As a consequence, it is difficult to translate the acid neutralising capacity given in mol eq. H^+ to mol CO_2. As a conservative starting point 2 mol eq. H^+ = 1 mol CO_2 is taken.

[13] Situation in the Netherlands.

[14] (AOO *et al.*, 2001).

[15] Construction and demolition waste is a very diffuse and often inhomogeneous waste stream. These properties complicate the use of C&D-waste as feedstock for mineral CO_2 sequestration. For the same reason, it is difficult to estimate the sequestration capacity of this stream, which is potentially large; for concrete, a 0.5% sequestration capacity of the total Japanese CO_2 emissions is estimated if 50% of all residue concrete is used (Fujii *et al.*, 2001). In our calculations we used cement as model component for C&D-waste.

[16] (De Wilde *et al.*, 2002)

The overall capacity of CO_2 sequestration in solid residues is limited. Although industrial residues are generated on a large scale, the scale of CO_2 emissions is simply much larger (about 180 Mton in 2001 in The Netherlands). However, for specific niche applications, such as for industrial and energy production sites where besides large amounts of carbon dioxide also solid residues are produced, carbon dioxide sequestration in alkaline solid residues might be an attractive option. In addition, residues could be used as feedstock for the first mineral CO_2 sequestration plants in order to enhance a technology breakthrough given their availability at low costs and near CO_2 sources and their relatively high carbonation reactivity.

4.2 Final selection of residue for further research

The selection of a residue for mineral CO_2 sequestration has been performed according to the requirements discussed in chapters 2 and 4. On the basis of the limited set of data presented in this report, for carbonation experiments at the Energy Research Centre of The Netherlands first steel slag and second possibly MSWI bottom ash are selected. The first is selected because of its high potential carbon dioxide sequestration capacity. The second is taken because of the large amounts in which this material is generated. For the moment, construction and demolition-waste has not been selected because of its inhomogeneous character.

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Appendix A   Examples of total composition of residues

Table A.1   *Total composition of selected residues*[17]

Residues	MSWI	C&D-waste		
Composition [g/kg]	Bottom ash[18]	Fly ash[19]	APC residue[20]	Cement[21]
Calcium	73.8 – 94.6	109.5 – 125.4	46.3	448.8 – 424.7
Magnesium	11.4 – 12.8	12.0 – 14.8	<1.1	9.0 – 11.0
Silicon	222.0 – 308.0	180.0 – 213.0	38.0	89.3 – 95
Aluminium	31.8 – 37.2	48.8 – 77.4	20.8	13.0 – 35.2
Iron	28.6 – 106.3	14.4 – 19.2	<1.6	10.0 – 24.0
Sodium	20.0 – 31.4	15.7 – 25.3	84.0	1.3
Potassium	8.5 – 11.1	24.2 – 31.2	109.0	6.4
Chlorine	1.1 – 3.1	38.0 – 49.9	232.0	< 0.5
Native pH [-]	9 – 11.5	7 – 11.5		12.4 – 13.0
ANC[22] [mol eq H$^+$/kg]	0.5 – 1.01	2.5		3.3

[continued]

Residues	Coal power plant	Slags		
Composition [g/kg]	Bottom ash[23]	Fly ash[24]	Phosphor[25]	Steel slag [26,27]
Calcium	25.1 – 95.6	22.2 – 70.4	332.2	222 – 250.8
Magnesium	11.3	5.5 – 18.6	5.1	45 – 69.9
Silicon	237.0	230.0 – 268.9	213.0	132.0
Aluminium	143.2	93.4 – 138.1	14.5	85.1
Iron	46.0	36.9 – 124.0	600.0	25.8
Sodium	13.1	4.8 – 7.8	6.2	4.1
Potassium	2.5	10.3 – 20.9	1.8	3.4
Chlorine	< 0.5		0.6	< 0.5
Native pH [-]	10.2	4 – 11.5	10.2 – 12.6	11.5 – 12.6
ANC [mol eq H$^+$/kg]	4.4	0.01 – 1	6.5 – 9.4	6.1 – 10.9

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[17]   The total composition is measured with ICP. Only the concentrations of calcium, magnesium, aluminium, iron, sodium, silicon, chlorine and potassium are shown.

[18]   Total composition (TC): (Meima & Comans, 1997), pH: (Sloot van der *et al.*, 2001) ANC: (Sloot van der *et al.*, 2001).

[19]   TC: (Groot de *et al.*, 1990), pH: (Sloot van der *et al.*, 2001) , ANC: (Sloot van der *et al.*, 2001).

[20]   TC: (Eighmy *et al.*, 1995).

[21]   Portland. cement is taken as example material. TC: (Short *et al.*, 2000), pH: (Sloot van der *et al.*, 2001), ANC: (Sloot van der *et al.*, 2001).

[22]   Acid Neutralization Capacity.

[23]   TC: (Groot de *et al.*, 1990), pH: (Sloot van der *et al.*, 2001) , ANC: (Sloot van der *et al.*, 2001).

[24]   TC: (Schramke, 1992), pH: (Sloot van der *et al.*, 2001) , ANC: (Sloot van der *et al.*, 2001).

[25]   TC: (Groot de *et al.*, 1990), pH: (Sloot van der *et al.*, 2001), ANC: (Sloot van der *et al.*, 2001).

[26]   pH: (Sloot van der *et al.*, 2001; Huijgen *et al.*, 2004), ANC: (Sloot van der *et al.*, 2001).

[27]   (Yan *et al.*, 2000).

Appendix B Process conditions for carbonation of alkaline solid residues

Table B.1 *Examples of process conditions reported for carbonation of alkaline solid residues*

Residue	Details carbonation process	T [°C]	p_{CO_2} [bar]	d [mm]	Time [h]	CO_2 uptake [gCO_2/kg]	(Ca)-conversion [%]	Reference
Blast furnace slag		25	3	N.A.	24	3	9% to calcite	(Johnson, 2000)
Cement-immobilised slag material	Supercritical CO_2	50	250		0.25	14.83		(Ginneken van et al., 2002)
Clean coal technology ash	5-50% moisture	25-50	3.5-8.6 (partial 20-100%)	N.A.[28]	24-72			
Coal fly ash	Aqueous route with 0.5M Na_2CO_3/0.5M $NaHCO_3$ and 1.0MNaCl. Slurry.	185	115	N.A.	0.5		84% to carbonates	(Fauth, 2001)
Coal fly ash	20% mositure.	25	2.8	<0.25	120	17.2 67.5		(Reddy et al., 1994)
Deinking ash		25	3	N.A.	24	170	17% to calcite	(Johnson, 2000)
FBC coal ash	Aqueous route with 0.5M Na_2CO_3 / 0.5M $NaHCO_3$ / 1M NaCl	155	75	N.A.	1	159	51	(Fauth et al., 2002)
FGD coal ash	Aqueous route with 0.5M Na_2CO_3 / 0.5M $NaHCO_3$ / 1M NaCl	185	115	N.A.	1	191	72	(Fauth et al., 2002)
MSWI ash		25	3	N.A.	24	60 – 140	39 – 50% to calcite	(Johnson, 2000)
MSWI bottom ash[29]	Aqueous route. Water content: moisture.	20 40 50	60 (liquid CO_2) 150 (supercrit. CO_2) 250 (supercrit. CO_2)	<10	1 1 1	15 20 20		(Devoldere et al., 2000)

[28] N.A. = not available

MSWI bottom ash[30]	10 mlH$_2$O / gMSWI	20	Atmospheric	N.A.	72-96			(Meima & Comans, 1997)
OPC cement		25	3	N.A.	24	22	22% to calcite	(Johnson, 2000)
Portland cement pastes[31]	W/c: 0.6.	59	97	N.A.	24	162		(Short et al., 2000)
Pulverised fuel ash	Water:solid 0.1 – 0.2	25	3	N.A.	24	15	57% to calcite	(Johnson, 2000)
Spent oil shale	20% mositure.	25	2.8	<0.25	120	37.5 19.6		(Reddy et al., 1994)
Stainless steel slag		25	3	N.A.	24	210	21% to calcite	(Johnson, 2000)
Steel slag (LD)	Aqueous route. 10 ml H$_2$O / g slag	200	20	<0.106	0.5	148	70	(Huijgen et al., 2004)
Waste concrete			low	N.A.			80% of calcium	(Kamiya et al., 1998)
Waste Dravo-Lime	Aqueous route with 0.5M Na$_2$CO$_3$/0.5M NaHCO$_3$ and 1.0M NaCl. Slurry.	185	115	N.A.	0.5		10% to calcite	(Fauth, 2001)

[29] Magnetic separation ferrous fraction
[30] Only free lime is used
[31] Dry samples showed no conversion.

Appendix C   Specific carbon dioxide sequestration capacity

Table C.1   *Specific potential carbon dioxide sequestration capacity on the basis of the acid neutralising capacity (ANC) of selected residues[32]*

Residue	ANC [mol eqH$^+$/kg]	CO$_2$ [g/kg]
Cement	3.30	72.5
Construction residue	1.62	35.5
MSWI air pollution control residue	1.91	42.0
MSWI bottom ash	0.5 – 1.28[33]	11.0 – 28.2
MSWI fly ash	2.5	55.0
Steel slag	7.8	171.6

Table C.2   *Potential CO$_2$ sequestration capacity on the basis of the elementary composition of selected residues.*

Residue	Ca [g/kg]	Mg [g/kg]	CO$_2$ [g/kg]
Carbon enriched fly ash	6.9	2.8	12.6
Cement	424.7 – 448.8	9.0 – 11.0	486.1
Coal fly ash	38.1	9.2	58.6
Electricity bottom ash	69.6	11.3	96.8
MSWI air pollution control residue	46.3	1.1	52.8
MSWI fly ash	119.1	13.5	155.2
MSWI-bottom ash	79.4 – 117.4	11.7 – 17.7	108.4 – 161.0
Phosphorus slag	332.2	5.1	373.9
Steel slag	222.0 – 312.5	45.0 – 73.1	325.2 – 407.1

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[32]   A selection of data has been made. Only alkaline solid residues with carbon dioxide sequestration potential are shown.

[33]   Johnson *et al.* found ANC$_{7.5}$ 1.2 - 1.7 ± 0.05 m eq/g (Johnson *et al.*, 1995).