

## Accelerated carbonation of stainless steel slag

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### Abstract

Ground stainless steel slag can be reacted with carbon dioxide gas in the presence of water at ambient or raised pressures. The precipitated, calcium carbonate, reaction product cements the slag particles together forming a monolithic structure. Additionally, carbonation alters the buffering behaviour of the slag and reduces the amount of leachable chromium and other metals.

In the present work, a stainless steel slag ( $<125\mu\text{m}$ ) was mixed with 7.5, 10 and 12.5 weight percent water and compacted to form small, cylindrical samples with bulk densities of 1550, 1650 and  $1750\text{ kg/m}^3$ . These samples were then exposed to a pure carbon dioxide gas for 1, 24 or 72 hours. Control cylinders were sealed in air for 28 days. After exposure to carbon dioxide, the samples were stored sealed in plastic bags until 28 days after manufacture and then tested for unconfined compressive strength and carbonate content. The broken samples from compression testing were then dried and ground for leach testing using both distilled water and acetic acid following the toxicity characterisation leaching procedure (TCLP).

Greater compaction and longer carbonation times are found to increase the strength of cylinders. Variations in the initial water content had no significant effect on the strengths obtained, which, for samples with an initial density of  $1750\text{ kg/m}^3$  after 72 hours of carbonation, were 9 MPa. Non-carbonated, control samples had negligible strength.

The amount of carbon dioxide, bound into the samples, was found to be independent of the degree of compaction and was a function of the moisture content of the samples. The cylinders containing the greatest proportion of water absorbed the most gas, independent of carbonation time. Although the samples continued to absorb  $\text{CO}_2$  up to 72 hours, 75% of the final carbonate content was produced within 1 hour and 90% by 24 hours of exposure. No carbonation reaction was observed for the control samples.

Leach testing, using distilled water and acetic acid-based tests, showed improved retention of chromium in the carbonated slag compared with the control samples. A value of  $0.02\text{mg/l Cr}$  was recorded in the TCLP leachates for the carbonated sample compared with  $0.31\text{mg/l}$  for the non carbonated control.

The results of this work show that stainless steel slag may be treated by accelerated carbonation to produce a product with engineered properties and reduced metals leaching.

## Introduction

The manufacture of stainless steel leads to the production of a slag with variable composition. This is due to the different processes used and the many different alloying elements that may be required in steel production. The variable nature of the waste and the presence of heavy metals, including chromium, mean that the wastes are difficult to dispose of and may present a threat to the environment.

The landfill directive [1] requires treatment of wastes prior to disposal and encourages the reuse or recycling of waste generally. In the U.K. the landfill tax provides a further economic incentive for a reduction in the volume of waste being sent to landfill. Stainless steel production also leads to the emission of carbon dioxide both directly from the furnace and indirectly from power requirements. Although not a major contribution to the total anthropogenic output of this greenhouse gas, its production at the same site as the waste slag may present an opportunity to combine the two waste streams in a controlled manner. Slag is known to react slowly with carbon dioxide from the atmosphere as part of the natural weathering process leading to the formation of calcium or other carbonates.

Another group of materials known to react with carbon dioxide, are those based upon ordinary Portland cement [2]. Studies of the long term performance of these materials, investigated accelerating this process by the application of high concentrations of the gas [e.g. 3]. It has also been found that freshly mixed cement pastes or concrete can be hardened in a matter of minutes by the application of CO<sub>2</sub> [4]. Investigation of the different mineral components involved and other similar materials has shown that both hydraulic and non-hydraulic phases can be reacted in this way [5] although an amount of water is necessary as a reaction medium. In particular, this study showed that the very poorly hydraulic  $\gamma$ -polymorph of dicalcium silicate was found to be reactive with respect to CO<sub>2</sub>. This phase is commonly found in stainless steel slag and is responsible for its dusty nature and wide grading curve. The  $\gamma$ -polymorph of dicalcium silicate undergoes a large volume change as a consequence of the reconstructive phase transformation from  $\beta$ -dicalcium silicate upon cooling at  $\sim 530^\circ\text{C}$  [6]

It has previously been demonstrated that the stainless steel slag will combine with carbon dioxide, gaining 20% of its own weight in 1 hour [7]. This degree of reaction is comparable to that achieved when OPC based materials have been cemented by accelerated carbonation [8]. Therefore, the feasibility of cementing the waste in this manner was investigated. With OPC-based materials, the water content and porosity of samples have been shown to be important controls upon the extent of the carbonation reaction. Low porosity or high water contents lead to the pores becoming blocked with either reaction products or water, which impede the intrusion of further CO<sub>2</sub> into the sample and slow the reaction.

A further consequence of the carbonation of calcium silicate based materials is that the chemical environment within the material is altered. In concrete this manifests itself as a lowering of the porewater pH which leads to the breakdown of a protective layer on the surface of reinforcing steel. This allows the steel to begin to corrode and eventually weakens the concrete. Carbonation has also been investigated in OPC based stabilisation/solidification of waste and the presence of carbonates has been found to alter the buffering ability of the system and alter the rate at which harmful components of the waste are leached [9,10]. To investigate how the carbonation of the slag alters its potential environmental performance the samples generated as part of the cementation experiment were leach tested and their acid neutralisation capacity investigated.

## Materials and Methods

The stainless steel slag used in this study was produced by Avesta Ltd and has the bulk composition given in Table 1. The slag contains the mineral phases: gamma dicalcium silicate  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>; merwinite - Ca<sub>3</sub>Mg[SiO<sub>4</sub>]<sub>2</sub>; akermanite - Ca<sub>2</sub>[MgSi<sub>2</sub>O<sub>7</sub>] which contains aluminium by coupled substitution with Mg and Si; periclase – MgO; Cuspidene - Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub> and chrome spinel - MgCr<sub>2</sub>O<sub>4</sub>. Also present are a quantity of stainless steel fragments.

Table 1. Composition of stainless steel slag used (weight percent)

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Na <sub>2</sub> O	F	SO <sub>3</sub>	LOI (1000°C)
46.66	27.92	2.91	9.75	1.22	2.76	1.23	0.26	1.59	0.43	4.28

The as-received slag contained particles up to 40mm in diameter, which were ground to pass a 125µm sieve. Large (up to 5mm) droplets of stainless steel were released from the slag during grinding and were removed. The slag was then mixed at three different water to solid ratios (0.075, 0.1 & 0.125) and compacted to form cylindrical samples (height 28mm, diameter 28mm) with three different bulk densities (1550, 1650 & 1750kg/m<sup>3</sup>). The water contents chosen were based around that found to be optimal for the reaction of the slag as a loose powder [7]. The densities, chosen by simple trials, varied from the minimum necessary for the fresh compact to retain its integrity under handling to the maximum required for the samples to be removed intact from the mould.

For each batch of samples, six cylinders were formed, half of which underwent the carbonation procedure. Immediately after forming, the remaining control cylinders were stored in a sealed environment. No attempt was made to exclude CO<sub>2</sub> from the control samples as the level of natural carbonation was expected to be negligible compared with that of the reacted samples. Carbonation was carried out in a sealed reaction chamber pressurised to 3 bar with ~100% CO<sub>2</sub>. The chamber contained a saturated NaCl solution in order to maintain a constant relative humidity around the samples. The carbonation reaction is exothermic and the heat released during the reaction was allowed to dissipate naturally. Samples remained in the reaction chamber for either 1, 24 or 72 hours and were then stored in an identical manner to the control cylinders.

On the 28<sup>th</sup> day after manufacture, the cylinders were tested for unconfined compressive strength using an Instron 1195 fitted with a compression cell and operating with a crosshead speed of 1mm/min. The broken samples were immediately dried and then ground to ensure that a small representative sample could be taken from each cylinder for x-ray diffraction (XRD) (Siemens 500 x-ray diffractometer - Cu K $\alpha$ -radiation) and thermo-gravimetric analysis (TGA) (Stanton Redcroft STA-780 thermal analyser attached to a PICO ADC-16 high-resolution data logger). The remaining carbonated samples were combined and well mixed to form a large sample for leach and acid neutralisation capacity testing.

The two leach testing procedures used were the US EPA toxicity characterisation leaching procedure (TCLP) [11] and the German DIN 38414 [12]. Both tests were scaled down to accommodate the small volumes of sample available. For the TCLP test, 200ml of weak acetic acid solution were rotated with 10g of sample for 18hours, and for the DIN test 200ml of distilled water and 20g of sample were used with a contact time of 24hours. The pHs of the leachates were recorded prior to filtering and analysing for major and trace elements.

The acid neutralisation capacity (ANC) test [13] was used in a modified form by allowing the CO<sub>2</sub> liberated from the carbonated samples to escape to the atmosphere [14]. For the ANC test, eleven 5g samples of the slag were placed with 30ml of varying concentrations of nitric acid. The concentrations ranged from 4N to zero in equal steps. After 48 hours on a shaker table, the pH of the solution was recorded and the leachate filtered and analysed for metals content.

## Results

The unconfined compressive strengths recorded are shown in figure 1. The carbonated samples had higher strengths than the control samples. The benefit of greater compaction of the initial sample is also clear. There is also a less pronounced increase in strength in the samples as the duration of the carbonation step increases.

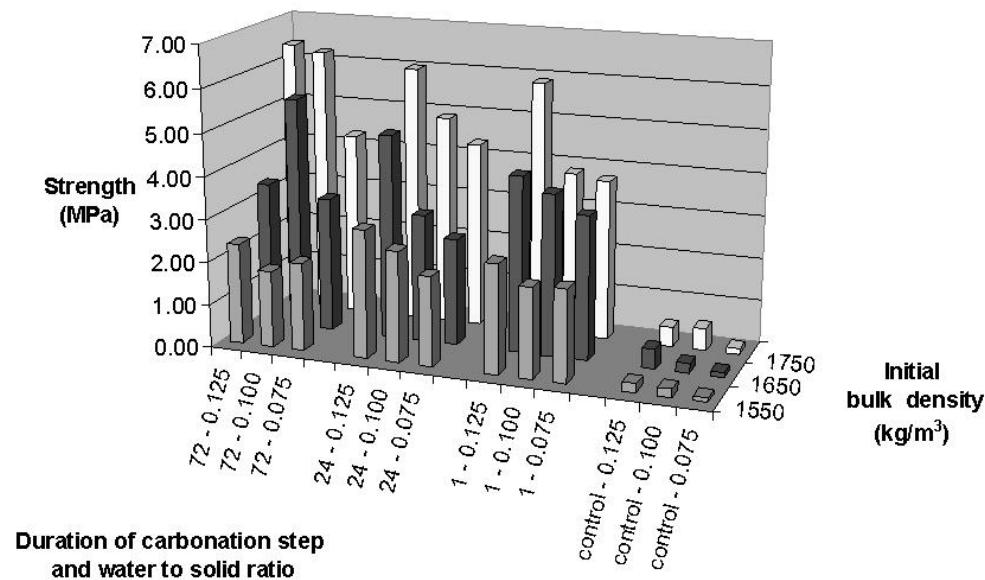


Figure 1. Unconfined compressive strengths of the compacted slag samples after 28 days.

The TGA traces for the samples formed with a w:s of 0.1 and compacted to 1750kg/m<sup>3</sup> are shown in figure 2, alongside a trace for the slag as received. The control sample shows a slight alteration especially in low temperature weight loss below 450°C. The three carbonated samples, however, show increasing alteration with greater reaction time. This increased reaction is seen in both low temperature weight loss and in the higher temperature region, which is usually ascribed to the breakdown of carbonates. The weight loss between 450°C and 900°C was measured for all the samples and used as an indication of the amount of carbonate present; the results of this are presented in figure 3. Figure 3 shows that there is little or no difference in the degree of reaction when the bulk density of the sample is changed. There is, however, a clear increase in reaction in response to increasing water content. All combinations of compaction and w:s are found to continue to react further with longer exposure periods in the reaction chambers. Approximately 75% of the total reaction seen in the samples carbonated for 72 hours is seen in those samples reacted for just one hour and ~90% of this value is reached after 24 hours.

Examination of the XRD traces (figure 4) before and after carbonation shows that three phases are obviously diminished as a result of the carbonation reaction. The dicalcium silicate, portlandite and periclase all have absent or diminished peaks after carbonation. The only new phase formed is calcite, although the largest peak for this phase at  $\sim 29.4^\circ$  overlaps the strong cuspidine peak in the same region.

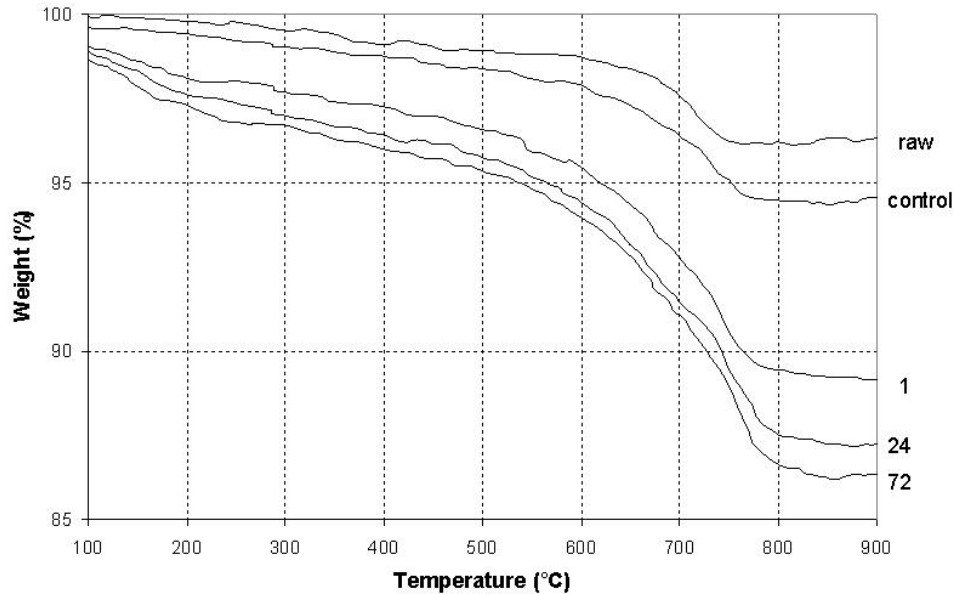


Figure 2. Thermogravimetry curves for the  $1750\text{kg/m}^3$  samples. Non-wetted raw slag for comparison.

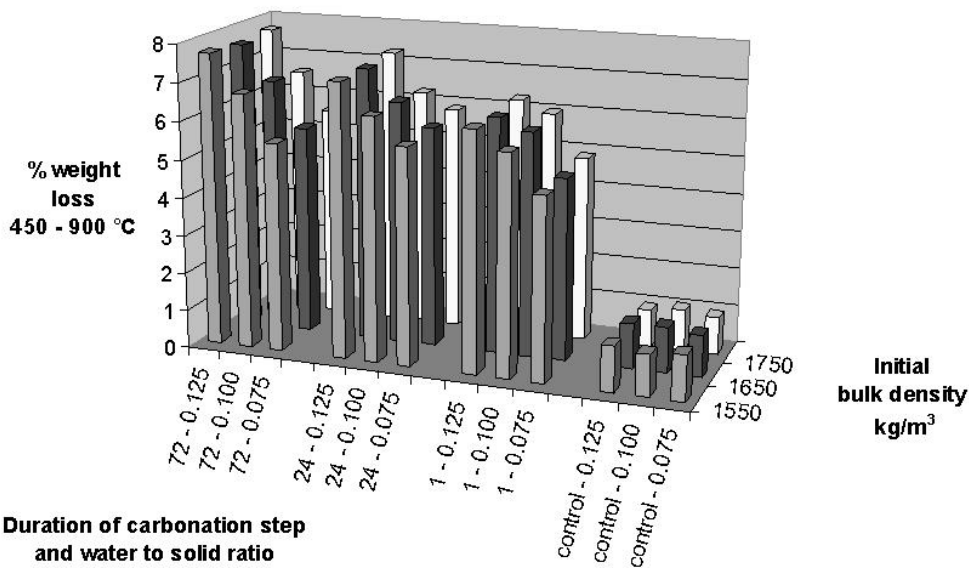


Figure 3. Weight loss of ground samples between  $450$  and  $900^\circ\text{C}$ .

The final pHs of the leachates for the ANC and leach tests are shown in figure 5. The pHs of the carbonate bearing solutions are seen to be lower for both leach tests and for the lower acid

additions of the ANC samples. Both the control and carbonated samples then show a plateau, where the pH is buffered to ~8, before there is an abrupt change to acidic leachates between an acid addition of 7.2 meq/g and 9.6 meq/g. The release of chromium in response to these three tests is shown in figures 6 and 7. In figure 6 the concentration of chromium in solution for the same acid additions are compared. At low acid additions the carbonated samples show a much lower concentration of Cr in solution. This is particularly true for the TCLP leach test where the non-carbonated samples show an order of magnitude higher concentration in solution (0.31 compared to 0.02 mg/l). The effect is less pronounced for the DIN test (0.48

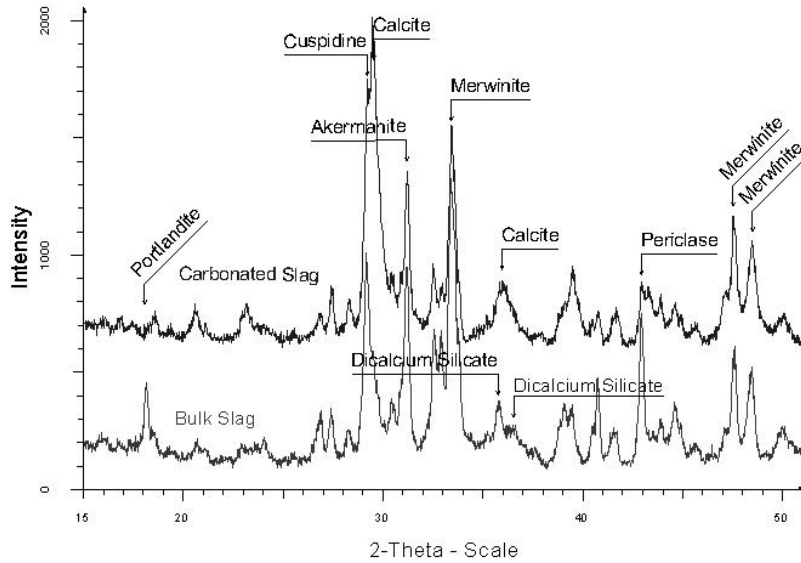


Figure 4. X-ray diffractogram of untreated ground slag and 72 hour carbonated slag.

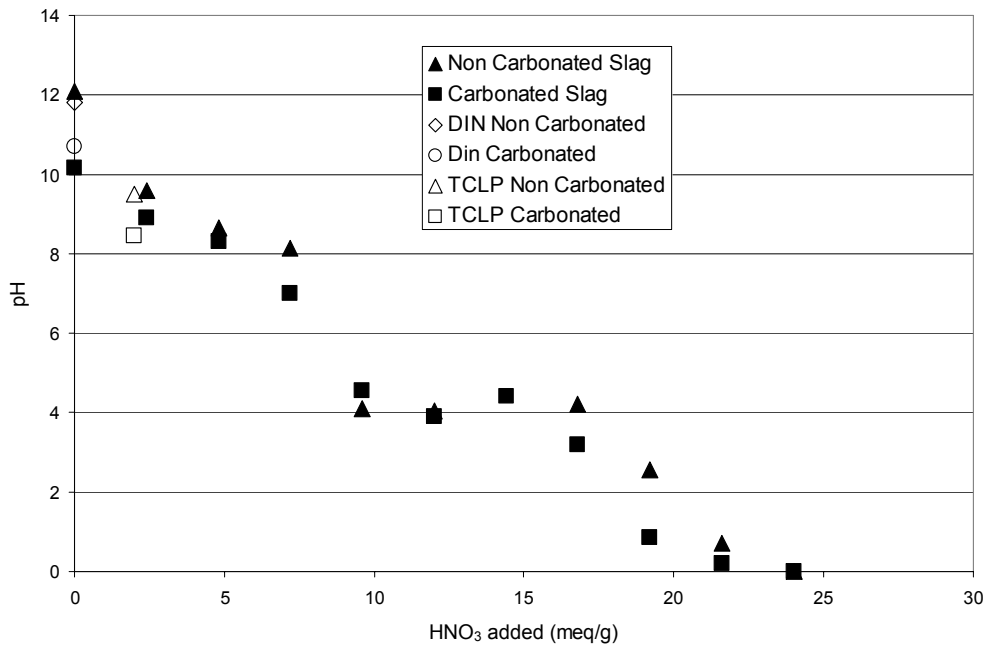


Figure 5. Eluate pH in response to acid addition after 18 hours TCLP, 24 hours DIN and 48 hours ANC.

compared to 0.08mg/l). Figure 7 shows that this is not purely a function of the different pHs of eluates as the Cr concentrations of the carbonated samples fall below those of the non carbonated samples independently of the test used, although this effect is restricted to pH>8.

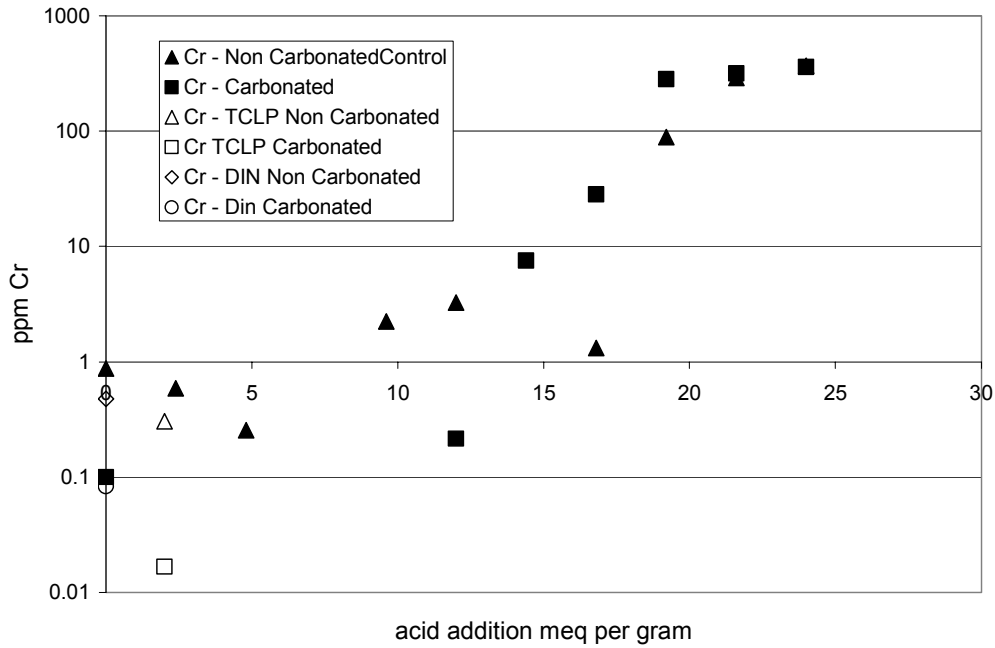


Figure 6. Chromium concentration of eluates in response to acid addition.

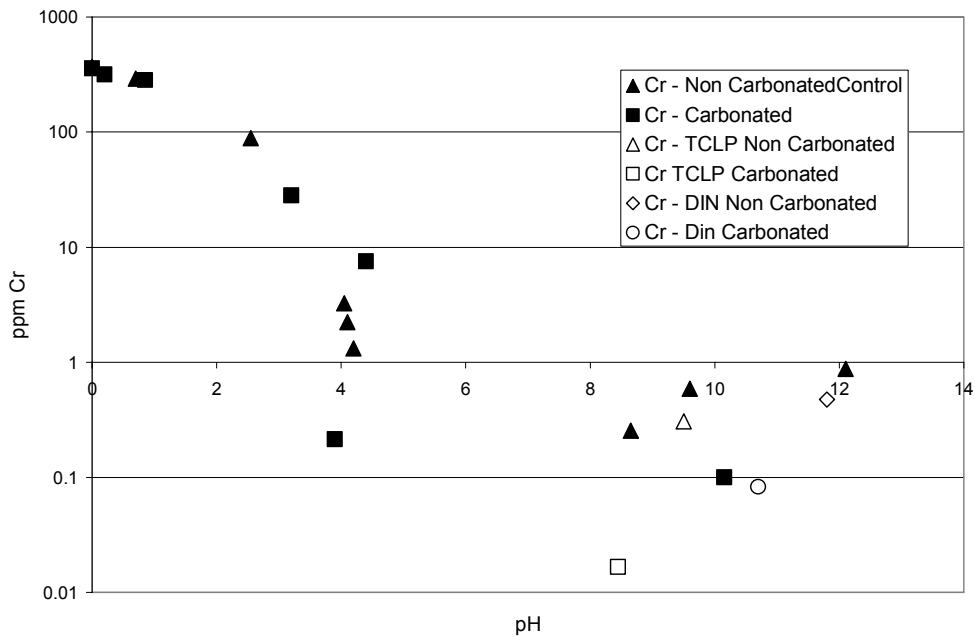


Figure 7. Chromium concentration in eluates as a function of final pH.

### Discussion

The continued strength gain and increasing carbonate content of the samples with increasing reaction time contrasts with previous experience with OPC and pure phase calcium silicates,

where after initial rapid strength development further reaction is limited [8]. A possible explanation for this is the presence of magnesium in the slag. Magnesium is known to significantly slow the precipitation rate of calcite in geological and environmental settings [15].

The formation of calcite from the  $\text{CO}_2$  and calcium from the  $\gamma$ -dicalcium silicate leaves the question of the fate of the silicate. No evidence is seen of other new crystalline phases being formed. Previous workers have suggested that accelerated carbonation produces a decalcified amorphous silica product [16]. However, in this study there is no evidence for an amorphous phase in the XRD results.

The beneficial effect of carbonation upon the level of chromium in the alkaline eluates is encouraging as it points to carbonation providing a stabilising effect upon the slags. The explanation for this effect is not clear, it is not thought to be a pH driven solubility phenomena as figure 7 shows that at the same pH the carbonated samples release less chromium into solution than the non carbonated controls. The chromium may be forming either a complex with the carbonate species introduced into the system or a new precipitate may be forming. Alternatively the surface coating of carbonate on the grains of the powdered slag may simply be providing a physical barrier to the dissolution of the chromium bearing phases. Before alteration the TCLP test shows a level of chromium in the eluate which is lower than the US EPA limit of 5mg/l. However the order of magnitude reduction afforded by carbonation is encouraging and the result of 0.02mg/l compares favourably with the US safe drinking water limit of 0.1mg/l.

An additional benefit of the carbonation reaction is the reduction in the free MgO content of the slag. Magnesium oxide can be a problematic in both disposal and reuse of waste materials as its hydration product brucite ( $\text{Mg}(\text{OH})_2$ ) has a much greater volume which can lead to damaging expansion. Therefore if this phase can be removed from the slag by carbonation a further undesirable property of the waste is removed.

## **Conclusion**

The carbonation of compacted cylinders of stainless steel slag forms calcium carbonate which cements the waste together. The reaction is initially rapid but continues upon longer exposure. Compaction of the initial powder sample reduces porosity and leads to increased strength in the product without diminishing the degree of reaction achieved. Carbonation reacts the poorly hydraulic  $\gamma$ -dicalcium silicate to form calcite and breaks down the potentially deleterious free MgO.

The reaction lowers the amount of Chromium leachable in response to the two standard tests used. Although the slag in its unaltered state does not exceed the regulatory limits for the leach tests used the reduction in the amount of chromium released are encouraging. This is seen to result from more than a simple pH dependant solubility effect, as is shown by the ANC results. Therefore the precise mechanism for this reduction requires further investigation.

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