

Using CaO- and MgO-rich Industrial Waste Streams for Carbon Sequestration

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1 Introduction

Climate change due to anthropogenic carbon dioxide (CO₂) emissions is a mounting concern. In order to reduce emissions in accord with the Kyoto Protocol and other mandates, a carbon tax is expected to be implemented. While no general agreement has been reached for the value of this tax, it is reasonable to expect the value to be in the range of \$10-60 per ton of CO₂.

Taking this carbon tax in its equivalent form, as a credit for carbon sequestration, we may be able to identify niche markets in existing industrial systems which are amenable to early adoption of a carbon sequestration scheme. In particular, there may be opportunities to use existing industrial waste streams with high alkalinity to sequester carbon in the form of stable carbonate minerals. We examine some relevant chemical and economic considerations for Steel Slag, a byproduct of steel manufacture, and concrete waste from construction and demolition projects.

These streams represent an opportunity to reclaim some of the carbon dioxide emitted during the manufacturing process. With concrete, for instance, energy was expended during the calcination process of cement manufacturing to separate carbon dioxide from calcium. This process accounts for about 50% of carbon dioxide emissions from cement manufacturing, which

in turn accounts for about 5% of global carbon dioxide emissions (Hendriks, et al, 1998). By re-carbonating the cement embedded in waste concrete, we can reclaim some of the CO₂ emitted in initial production.

Concrete has a wide variation in composition, but is generally 10-15% cement, with the remaining mass comprised of inert aggregate (e.g. gravel and crushed rock) and water. The cement portion contains calcium oxides (CaO) and hydroxides (Ca(OH)₂) which can be reacted with carbon dioxide dissolved in water to produce Calcite (CaCO₃) or other carbonate phases.

Steel slag is a consolidated mix of many phases, principally of calcium, iron, magnesium, and manganese. The proportions vary with the conditions and the feedstocks for the particular furnace where the slag is generated, but in general the dominant phase (40-50% by mass) is Portlandite (Ca(OH)₂). Calcium from the dissolution of the Portlandite in steel slag can be combined with carbon dioxide as for cement. Similarly, magnesium, making up a smaller, but still significant portion of steel slag, can bind with CO₂ to form Magnesite (MgCO₃).

Rough estimates of the carbon-binding potential of steel slag in Concrete are shown in Table 1¹. The experiments and analysis in the remaining sections are designed to assess the feasibility of making this conversion on an industrial scale.

Table 1: Estimated annual sequestration potential of concrete and ferrous slag in the United States

	ton CO ₂ / ton material	flow of material [Mt/yr]	Sequestration Potential [Mt/yr]	Percent of US CO ₂ output
Steel and blast furnace Slag	0.33	16.9	5.6	0.1
Waste concrete	0.05	68	2.9	0.05

Figure 1: Table 1: Estimated annual sequestration potential of concrete and ferrous slag in the U.S.

2 Methods

To assess the feasibility of extracting free calcium (Ca) from steel slag and concrete waste, a series of experiments measuring the dissolution of these materials in aqueous solution was performed.

A 500 ml cylindrical glass reaction chamber was filled with de-ionized water and a pH buffer, then bubbled with pure N₂ gas to eliminate dissolved CO₂. The chamber was stirred via a magnetic stir-bar at 450 RPM. A quantity of slag or concrete was added such that all calcium would be dissolved at

¹The estimate for the flow of waste concrete is highly uncertain since no formal reporting system captures the majority of construction and demolition waste. This is derived from EPA (1998). The true figure is probably much larger.

equilibrium at the highest pH tested, i.e. a total expected Ca concentration of 0.01 mol/l. The chamber was either sealed or kept at positive pressure of N₂ during the experiment to prevent intrusion of atmospheric CO₂ and subsequent formation of CaCO₃.

Slag and concrete samples were sieved into size fractions of particle diameter (D_p) between 45 and 74 μm , 74 and 300 μm , and 300 and 600 μm ². Solutions were prepared with buffers known to have negligible binding capacity with Ca and Mg. CAPS was used to hold a pH between 10.5 and 10.6, TES held a pH between 7.4 and 7.6, and unbuffered solutions ranged in pH from 10.8 to 12 over the course of the experiment.

Samples were taken periodically and immediately filtered through 0.45 μm syringe filters³ to separate the dissolved fraction. Total dissolved Ca was measured by titration with EDTA (Standard Method 3500-Ca-D).

Steel slag was run for several size fractions and several pH values. Experiments with concrete are incomplete, however the results for 45-74 μm particles in an unbuffered system are presented.

3 Results

Measurements of the dissolution of Ca from steel slag for several pH's and size ranges are presented in Figure 1. The dissolution of Calcium is more rapid for smaller particle sizes, and for lower pH. The data for slag particles with diameter between 45 and 74 μm at pH 7.5 are shown on linear scale in Figure 2. The dissolution curve has a hockey-stick shape, with rapid initial kinetics in the first hour or so, and then settling to a slower, log-linear rate. Approximately half of the Ca observed to dissolve does so within the first minute. By 160 hours, 230 mg of Ca per gram of slag has dissolved, which corresponds to 84% of the expected total Ca in the slag.

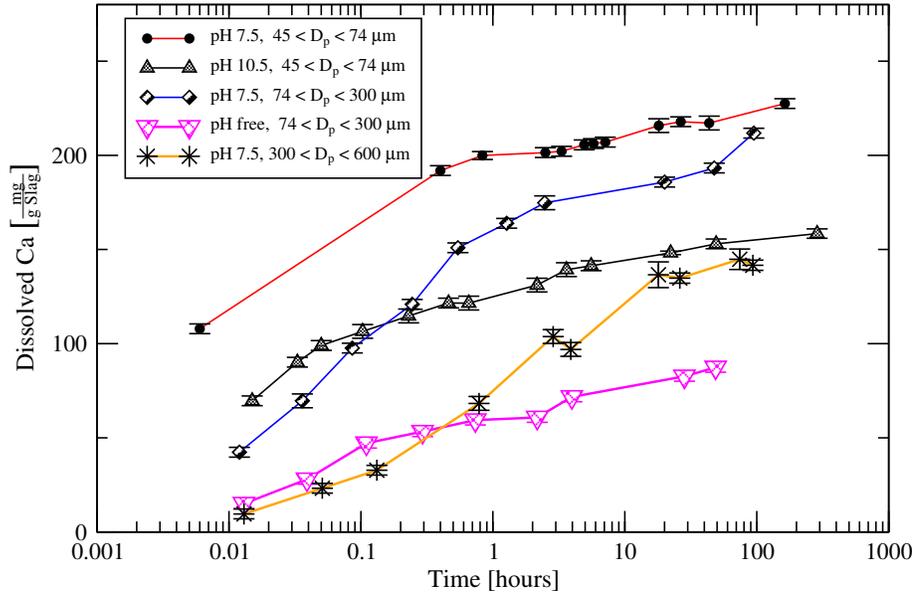
Both the extent and rate of dissolution become notably smaller for particles in the larger size ranges, however the dissolution rate is not as sensitive to particle size as simple theory would predict. For instance, the ratio of dissolution rates for the 45-74 and 74-300 μm size fractions, measured at 1 hour, is 1.25. However, we would expect dissolution rate to be proportional to specific surface area, holding pH and other variables constant. Using a hard-sphere approximation, the ratio of surface areas for these fractions is 2.4⁴. This discrepancy may be due to the heterogeneous composition or high porosity of slag particles.

²X-Ray Diffraction analysis confirms that the fine and course size fractions of slag are not chemically different.

³Additional 0.02 μm filtration and post-filtration acid-digestion were both found to have no effect on measured Ca concentration, indicating the presence of colloids in the filtered samples to be negligible.

⁴Fitting the slag particles to a log-linear particle mass distribution.

Figure 1: Dissolution of Calcium in Steel Slag



PH is also a strong determinant of dissolution rate. This is consistent with the theoretical dependence of dissolution rate on saturation state. The saturation state of $\text{Ca}(\text{OH})_2$, the dominant phase of Ca in slag, decreases (the solubility increases) as pH decreases.

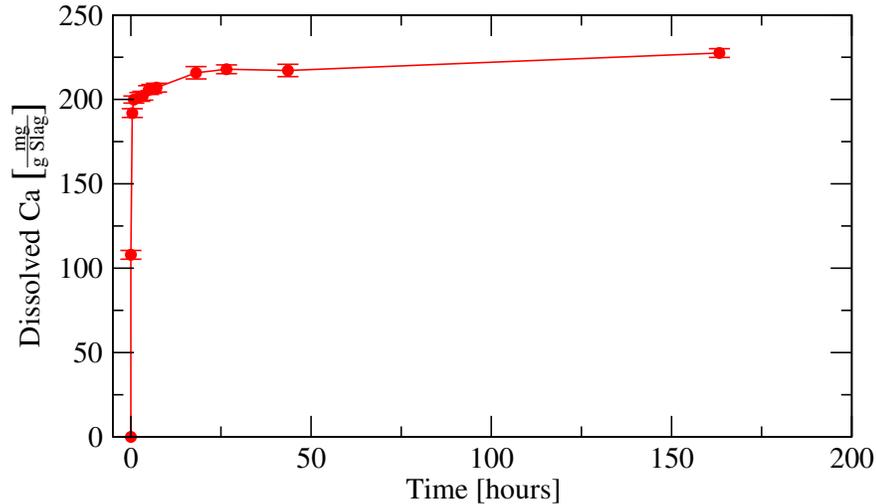
Although the set of experiments with concrete are not complete, data for 45-74 μm particles in an unbuffered solution are presented in Figure 3. The general shape of the curve is the same, with initial rate of dissolution similar to, if not faster than, steel slag. The quantity of dissolved calcium after 25 hours, 26 mg per gram of concrete, is estimated to be roughly 70% of the total Ca in the cement portion of the concrete.

4 Options for Steel and Iron Slag

Virtually all of the slag produced in the United States is currently sold and used for various applications, predominantly for asphalt and concrete aggregate and road base. The average market value for iron and steel slag at the plant was \$8.05 per metric ton in 2001 (Kalyoncu, 2001), equivalent to \$25 per ton of CO_2 . Given that likely CO_2 credits are of this order, this cost is probably prohibitive for a scheme where one buys slag solely for purposes of sequestration and then disposes of it.

Use of the slag for sequestration, however, does not necessarily exclude subsequent uses. A possible scheme for carbonation of slag is outlined in the

Figure 2: Calcium dissolution from steel slag
 pH 7.5, $45 < D_p < 74 \mu\text{m}$



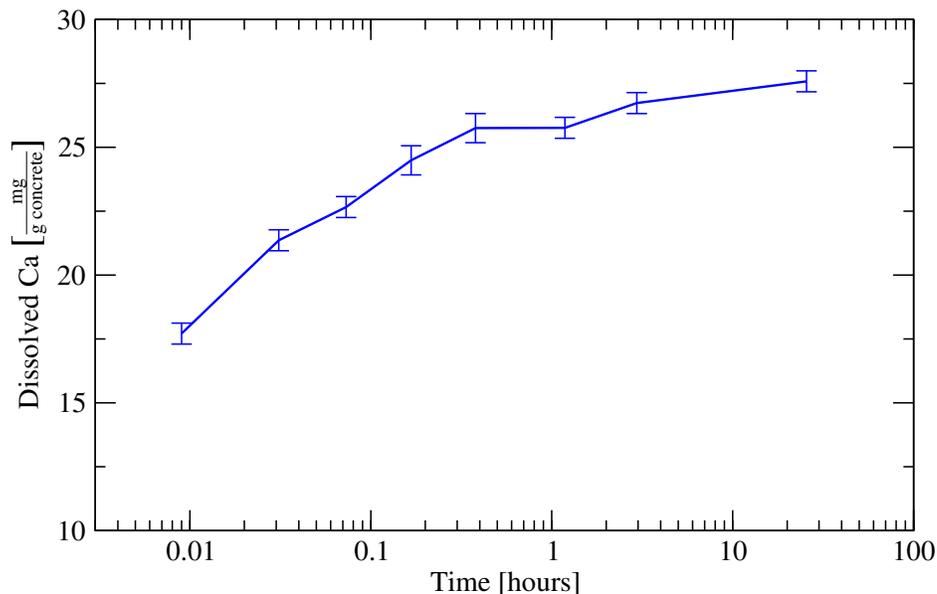
next section which is non-destructive⁵. Furthermore, there are two reasons why slag intended for other applications is amenable to intermediate use in a sequestration scheme.

Most applications for slag require that it be crushed and sieved into relatively small particles. Some applications, such as use as a cement additive, require extremely fine grinding. Since the sequestration process requires small particles, using slag crushed for these applications can avoid additional energy and cost of grinding specifically for sequestration.

Secondly, the dissolution of oxides from the slag may add value to the slag for use in the most common applications. Slag tends to have high water-absorption and expansion properties due to the hydration of Ca and Mg oxides over time (Kalyoncu, 2001). This is an undesirable property for concrete and asphalt aggregate, and for base and fill material (Turner-Fairbanks, 1994). This property would be eliminated in any kind of carbonation scheme. In fact, washing or weathering is often already required for slag used as road base (ibid.). A modification of this process to ensure capture of carbon may be all that is required to harness the sequestration potential of slag.

⁵We assume a 75% dissolution of Ca and Mg oxides from the slag, which would effect a 40% reduction in mass. However, the Ca and Mg carbonates formed may be mixed back into the slag for many applications, or may have market value as a separate product. This depends on the physical properties of the precipitate, which are currently unknown. For the purposes of the calculation we assume procurement and sale of the slag to be revenue-neutral.

Fig. 3: Dissolution of Calcium from ground concrete
 $45 < D_p < 74 \mu\text{m}$, pH unbuffered



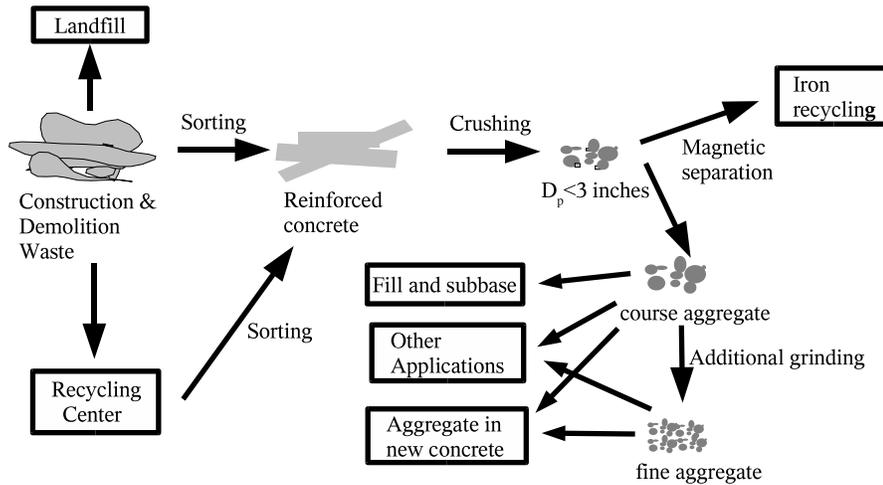
5 Options for Concrete

Reinforced concrete waste is the single largest component of demolition and construction waste. It is generally removed from demolished buildings, roadways, and other structures mixed with other sorts of rubble. While tipping fees at landfills are relatively low for concrete waste (which is considered "clean" waste), the extremely large quantities of it can make transportation and disposal expensive. About half of concrete waste is currently sent to landfills, while the rest is recycled in a variety of ways. The decision on whether to recycle, and how to recycle concrete waste, rests on the balance of tipping fees and transportation costs versus the cost of sorting and grinding and (possibly) transportation of the resulting material, minus the value of the recycled material. These costs vary regionally and are all of the order of dollars or a few tens of dollars per ton.

In large projects, much of the concrete waste is reused onsite as fill and subbase. It can also be used as aggregate in new concrete, obviating the need to import new aggregate. A limitation to this is that concrete made with recycled aggregate tends to absorb more water, expand more, and have slightly impeded performance characteristics compared with concrete made from new aggregate. This is due to hydration of the original cement particles.

If recycled concrete, after grinding and before final application, could be put through a carbonation scheme like the one described below, many

Figure 4: Management options for concrete waste



of its undesirable characteristics would be eliminated, adding value to the product. Additionally, the carbon capture scheme could be run without incurring the cost of additional grinding or interrupting major material flows. One can imagine a carbonation step being added to the recycling process at construction waste recycling facilities and large construction sites.

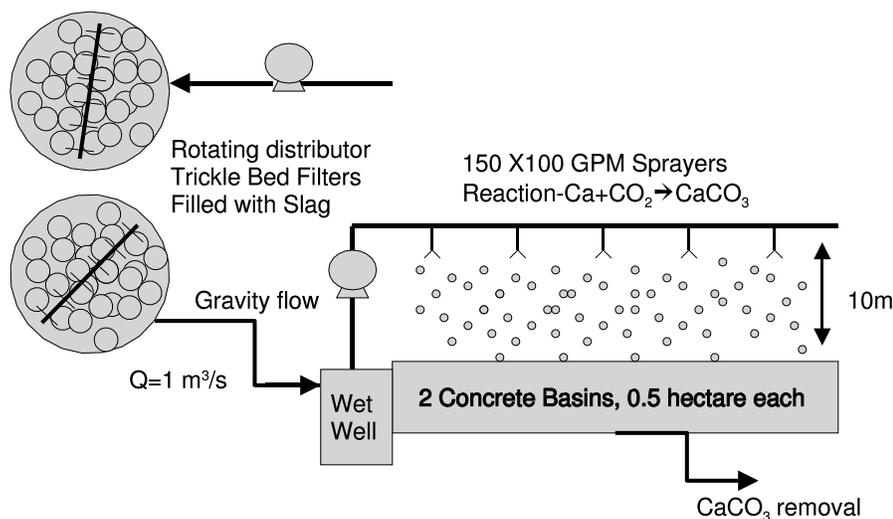
There may also be niches within the concrete industry that are particularly suited to sequestration schemes. For instance, after grinding, the concrete is often separated into course and fine fractions. The fine fraction has a disproportionate share of cement - about 40% - making it particularly undesirable for most applications. But the small particle size and high cement content make it ideal for carbonation. Once washed in a scheme like the example given, the fines fraction may have better market potential.

6 An example carbonation scheme

We will now assess the economics and energetics of a simple scheme for sequestering carbon using steel slag or concrete waste. A diagram of the scheme is shown in Figure 5. Water is trickled on a bed of ground slag or concrete via rotating distributors, allowed to pass through by gravity, and collected at the bottom. The solution is then pumped from a wet well through sprayers in order to contact the solution with CO_2 in the air, and then collected in a flat concrete pond where CaCO_3 and other solids can settle out.

Two beds and ponds are operated in parallel, allowing one set to be drained and unloaded while the other continues to operate. Materials can be collected and moved with standard front-loaders. We assume 5% downtime for maintenance and material exchange. Capital equipment and main-

Figure 5: Example Carbon Sequestration Scheme



tenance are priced for a 30 year lifetime.

For the purposes of this calculation, we assume that the flowrate and bed geometry have been chosen such that the solution exiting the bed is saturated with respect to calcium (900 mg/l, using clean input water⁶). We further assume 100% of Ca^{2+} goes to form CaCO_3 after contact with air, or further downstream.

The input water has few quality requirements. In fact, it is particularly advantageous to use acid waste streams, which would be neutralized by the slag and would speed the kinetics of dissolution⁷. For nonacid inputs, it is probably essential to utilize a natural or secondary industrial flow for this scheme, since the water demand is quite high - about $1 \text{ m}^3/\text{s}$, or 23 million gallons per day. If this water was obtained at a typical western agricultural water price of \$30 per acre-foot, it would add \$800k per year in expense. Cost of water procurement was not included in the calculations below.

The flow of materials is based on the CO_2 flux through the system, which has a square, hectare-sized footprint (107k ft^2), and a 10 m high capture area, at an average wind velocity of 3 m/s . An assumed capture efficiency for CO_2 entering the system of 50% fixes the water and mass flow requirements.

With these assumptions this scheme can sequester 32k tons of CO_2 per year, generating 73k tons of CaCO_3 per year. It requires a minimum of 97k tons of slag, 680k tons of concrete, or 200k tons of high-cement concrete fines per year.

Table 2 shows an estimated cost breakdown for the facility described, in-

⁶This was the measured dissolved calcium concentration in a saturated slag solution

⁷However, sulfur-based acid streams will bind some of the calcium that would otherwise be used for carbon sequestration.

cluding capital costs (annualized at 6% interest over 30 years) and operation and maintenance costs. For a carbon credit of \$20 per ton or more, it seems feasible to run such a facility. It should be noted, however, that this is a very rough analysis. There are still many unknowns on which the revenue-cost balance depends strongly. The cost of procurement and transportation of both water and raw materials will depend on local circumstances, and have potential to dominate the economics. The efficiency of CO₂ capture from air passing through the system, and the extent of available calcium dissolved from slag or concrete is also uncertain. We consider these to be optimization issues, and beyond the scope of this paper. However, from our rough analysis it appears that this sort of system is at least in the realm of possibility.

Table 2: Estimated construction and maintenance costs for example carbonation scheme

Item	Quantity	Annual cost
0.5 Hectare Concrete Basins	2	22000
100 HP Pump	8	44000
Piping	(all)	22000
Wet well	1	3600
Sprayers – 100 GPM	150	22000
Pump O&M	(all)	12000
Operator	1	60000
Front-loader and operation	18 days	13000
Electricity	5 GW-hr	300000
Total cost		\$500,000
Carbon credit revenue @ \$20/ton CO ₂		\$640,000
Carbon credit revenue @ \$40/ton CO ₂		\$1,280,000

7 Conclusions

While a great many unanswered questions remain with respect to the use of slag and concrete for sequestering carbon, it is clear that the idea is worthy of further inquiry. With current information, it seems reasonable that a profitable scheme of this kind can be constructed, but it also appears that no large scale, homogeneous system will be effective across-the-board. Effective application of carbon sequestration technology will probably become an exercise in industrial ecology, as it depends crucially on the matching of inputs and outputs from different industries, using existing flows and infrastructure, and clever rethinking of current practices. The potential value of carbon credit available from the flows in Table 1 is on the order of \$170 million annually, so this effort could be worthwhile economically. Socially, such endeavors are valuable as early implementations of carbon sequestration.

Such niche facilities will provide valuable technological experience, making the way for larger-scale operations.

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