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Review

The Recycling and Reuse of Steelmaking Slags - A Review

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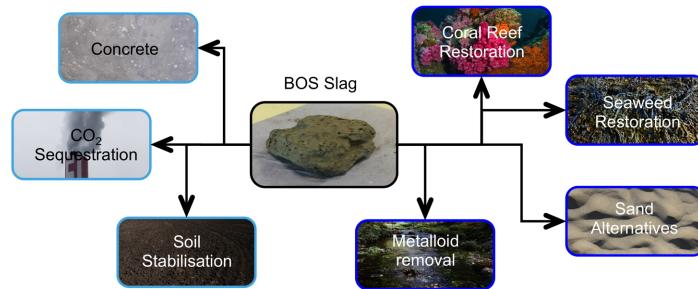
KEYWORDS: steelmaking slag; cement; coral reef; CO₂ sequestration; seaweed; phytoplankton

ABSTRACT

Large volumes of slags are formed as by-products during the refinement of pig iron by basic oxygen steelmaking or electric arc furnace steelmaking. In order to lower the environmental impact of the steel industry and ensure its economic sustainability, there have been significant studies finding the ways to recycle by-products. The formation, composition and physical properties of steel making slag are discussed with regard to the problems associated with its reuse. The volume instability caused by free lime exposure to moisture means that the reuse of steelmaking slag is often limited as many potential applications, and the leaching behavior of steelmaking slag is important for environmental considerations. Land-based applications that have been demonstrated include replacing natural sand as aggregate in cement, which may be combined with the CO₂ sequestration properties. Steel slag shows use as a liming material (when spread over acidic soils to help to raise the pH to a more neutral level) and to enhance the physical properties of soft soils. Potential benefits to the marine environment is due to high porosity and large surface area, making slags ideal

for coral reef repair (e.g., overcoming coral bleaching) and replacement (e.g., artificial reef to promote growth of green marine plants and seagrass), as well as a growth promoter for seaweed growth and phytoplankton are microscopic organisms that are an essential component of ecosystems in oceans around the world. The chemistry of steelmaking slag also makes it a contender for adsorption of H₂S and metalloids from marine environments.

GRAPHICAL ABSTRACT



1. Introduction

During the steelmaking process, various slags are produced as by-products (Shen and Forssberg, 2003). The first stage of steel production is blast furnace steelmaking, in which raw iron ore is converted into pig iron, which contains various amounts of carbon, silicon, manganese, sulfur and phosphorus. Due to the high carbon content, the material is extraordinarily brittle and unsuitable for secondary processes (e.g., rolling or shaping) (Biswas, 1963). Therefore, the pig iron must be refined by basic oxygen steelmaking (BOS), which produces slag by-product. Electric arc furnace (EAF) steelmaking, another form of secondary steelmaking also produces slag as a by-product. BOF and EAF slags are generically known as steelmaking slags. BOS slag is also known as BOF (basic oxygen furnace) slag, and the choice of acronym depends on the source material; however, herein we will use BOS as a default.

Around 20 million tons of slag is produced annually in Europe, half of which is produced is BOS slag (Liu et al., 2016), meaning that large quantities of industrial by-products are produced each year. One obvious alternative to landfilling such by-products would be to reutilize the slag in steelmaking or use for secondary applications (Joulazadeh and Joulazadeh, 2010). Records show that as early as 1589 steelmaking slag has been used to make cannon balls in Germany (Joulazadeh and Joulazadeh, 2010), and in the 1950's slag was utilized to stabilize riverbanks as well as railway ballast, artificial stone and acoustic and thermal insulation (Garside, 1956; Motz and Geiseler, 2001).

As part of a broader move to lower the environmental impact of the steel industry and ensure its economic sustainability, there are significant incentives to find ways to recycle slag by-products both to protect the environment and ensure the sustainability of the steel industry. Herein, we review approaches to the re-use of steel making slag, with particular focus on those that lower the environmental impact of industry, in the hope to promote further research and application of a material with potential as resource rather than a by-product.

2. Blast furnace steelmaking

Raw iron ore is characterized by the most abundant iron-containing mineral found in the ore: magnetite (Fe_3O_4), hematite (Fe_2O_3), siderites (FeCO_3), and limonites ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) (Walker, 1986). All the impurities in iron ore (silica, alumina, titania, sulfur, and phosphorus) are collectively known as *gangue*. All iron ore that is mined has to be crushed, and if the particles are of suitable size are directly charged to a blast furnace; however, if the particles are too fine, then they are processed in a sinter or pellet plant prior to introduction in a blast furnace (Walker, 1986).

During sintering, fine iron ore particles are mixed with a small amount of coal (5% by weight), and the mixture is then ignited (Peters, 1982). The process is driven by the decrease in surface energy (surface area) that causes the edge of the particles to fuse together (Fig. 1). The particles produced in this manner have a lower density than particles produced by a pellet plant (Walker, 1986).

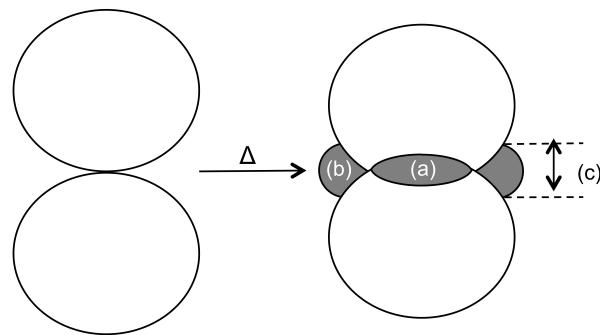


Fig. 1. Schematic diagram of the sintering of two particles that shows the reduction in surface area, a-lens, b-neck and c-shrinkage. (Walker, 1986). The presence of a liquid accelerates the process of bonding between particles, meaning that material may be transported from the lens area (a) to the neck area (b) by viscous flow.

The first step of the pelletizing process is known as *balling*. The ore is mixed with a binder (bentonite clay), and then placed into a rotating drum with excess

water. Where the particles come into contact, a liquid bridge between the particles is formed (Fig. 2); capillary suction occurs which bonds the particles together, first by flocculation and then agglomeration until small 'green' balls are formed, which have a low crush strength (2-4 psi) (Peters, 1982; Walker, 1986). Heating the pellets to 300 °C allows the excess water to evaporate, and heating to 1250-1350 °C results in consolidate of the pellets with a concomitant increase in crush strength (500-1000 psi).

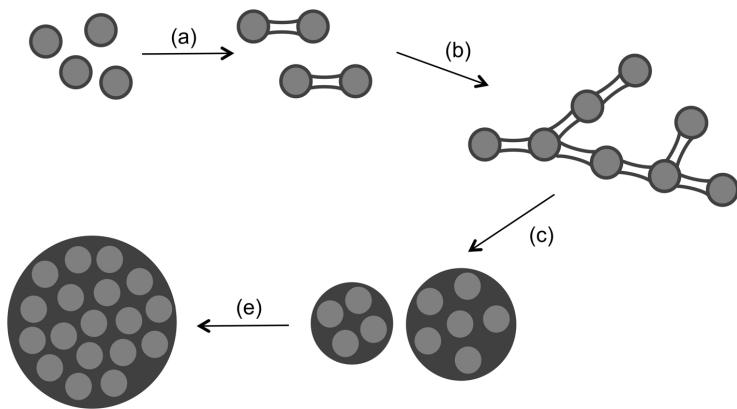


Fig. 2. Schematic diagram showing the processes for balling during the pelletization process: (a) liquid bridge formation, (b) flocculation, (c) agglomerate growth, and (d) spherical agglomerate formation.

Since the 18th century, coke has been the dominant fuel used in the blast furnace. Coke comes from heating coal in an airless atmosphere (*coking*) to remove any volatiles. The primary function of coke is to generate the heat required for blast furnace steelmaking. The combustion provides carbon and CO to chemically reduce iron oxides to elemental iron. The coke also provides structural support for the layers of iron ore in the furnace (Peters, 1982; Walker, 1986).

During the blast furnace process limestone (CaCO_3) flux is added, to collect the waste products produced: silica (SiO_2), phosphorus pentoxide (P_2O_5), calcium sulfide (CaS), magnesia (MgO) and alumina (Al_2O_3). This forms blast furnace (BF) slag, which floats on top of the surface of the hot metal (Peters, 1982). The blast

furnace is designed to work in a counter-current manner, meaning that the solid charge of ore and coke descends while the gases that are generated at the bottom of the furnace ascend. As the charge descends, it is chemically reduced resulting in swelling, as a consequence, the blast furnace slopes outwards in the stack of the furnace, see Fig. 3 (Coudurier, et al, 1978; Walker, 1986; Zhang, 2016; Xinliang et al., 2018; Gao, et al., 2014). After the charge has swelled, it begins to decrease in size as it changes into liquid iron so the bosh area the furnace (Fig. 3) begins to slope in again (Peters, 1982; Evans, 2015). Blast furnaces are generally over 50 m high and up to 14 m wide in the hearth area. A typical furnace produces 10000 tons of pig iron, 3000 tons of slag and dispose of $1.5 \times 10^6 \text{ m}^3$ of exit gas over a period of 24 hours (Coudurier et al., 1978).

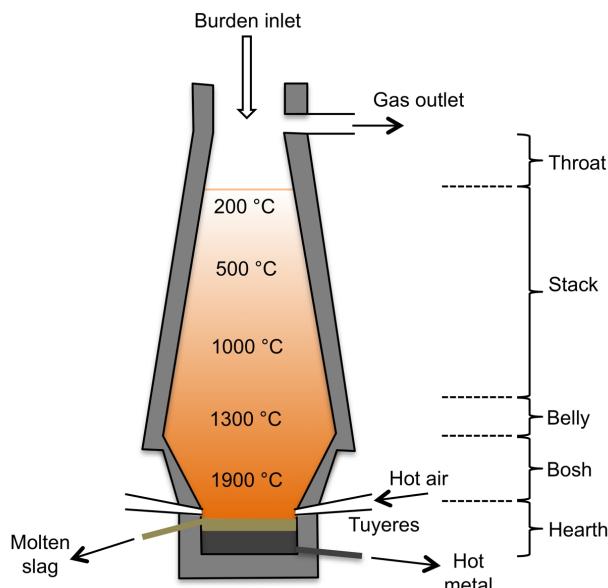


Fig. 3. Schematic diagram showing the features of the blast furnace design.

The overall chemical reaction that occurs in the blast furnace is that the ore is reduced to molten iron by the coke; however, in detail it is more complex. The carbon in the coke ignites (Eq. 1) in the area of the *tuyeres* (Fig. 3). As the carbon dioxide produced is in contact with incandescent coke it is reduced to carbon monoxide (Eq. 2). The CO produced travel upward and reacts with the iron ore

converting it from hematite via magnetite and wüstite (FeO) to metallic iron, Eq. 3-5.



The direct reduction of magnetite to iron (Eq. 6) only occurs once the system is in equilibrium and at low temperature, while the reduction of wüstite to iron by solid carbon (Eq. 7) occurs as the charge enters the bosh area of the blast furnace (Fig. 3). The direct carbon reduction reactions are endothermic, and more heat needs to be added to compensate for the loss of heat.



The gangue is also reduced in the blast furnace (Eq. 8-10). The phosphorus produced dissolves in the metal and has to be removed in the next stage of steelmaking. The silicon and manganese separate themselves between the metal and slag (Peters, 1982; Walker, 1986).



3. Basic oxygen steelmaking (BOS)

After pig iron is produced in the blast furnace process; the molten iron is sent

to the BOS furnace where it is combined with steel scraps and lime ($\text{CaO}/\text{Ca}(\text{OH})_2$) or dolomite ($\text{CaMg}(\text{CO}_3)_2$). The BOS method can manufacture 300 tons of steel in less than one hour. The most commonly used design is a cylindrical BOS vessel (Fig. 4), at the top of which is an open-topped cone (Shi, 2004), with a refractory lining made of periclase (cubic-MgO) (Barker et al., 1998; Peters, 1982; Barker et al., 1998). There is a tap hole on the side of the BOS vessel for sampling, tapping and disposing of slag. A tilting mechanism on the side of the BOS vessel allowing for several different functions: (a) if the vessel is tilted backwards at about 60° , then the vessel can be charged, or the steel can be sampled; (b) if the vessel is tilted back beyond 90° then slag is removed from the vessel; (c) the vessel can also be tilted 135° forwards then the steel can be tapped out through the taphole.

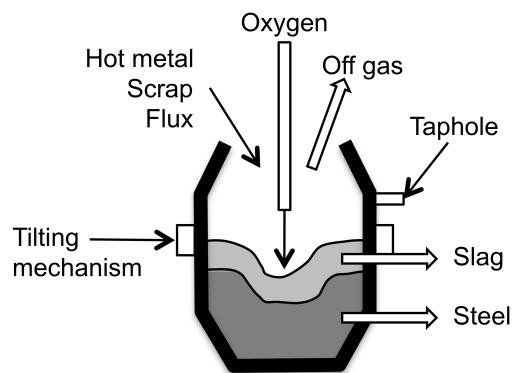
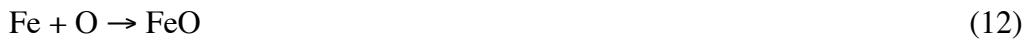
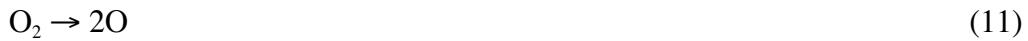


Fig. 4. Schematic illustration of a basic oxygen furnace.

Initially, steel scrap is charged to the furnace and then molten iron is placed on top (Singh, 2012). The addition of the steel scrap helps maintain the temperature of the furnace ($1600\text{-}1650\text{ }^\circ\text{C}$) allowing the necessary chemical reactions to take place. A water-cooled oxygen lance (Fig. 4) is lowered into the furnace and sits about 2 m above the surface of the molten metal. The lance blows 99% pure oxygen through the mixture at nearly supersonic speeds. Immediately after the oxygen lance has been lowered either lime or dolomite are added, which combine with unwanted elements to form slag (Brandt and Warner, 2005). Initially, as the oxygen is being blown through the charge, three separate oxidation reactions take place (Eq. 11-13).



The distribution of the oxygen between the metal and slag is controlled by the lance height and oxygen flow rate. The most important reaction that takes place is the removal of carbon (Eq. 14 and 15).



Fig. 5 shows how the concentrations of different elements change in the furnace change during the oxygen blowing process. Carbon oxidation is a critical reaction as the reaction produces large amounts of CO and CO₂ gases that help to agitate the bath and aid in the removal of hydrogen, nitrogen and some of the non-metallic inclusions.

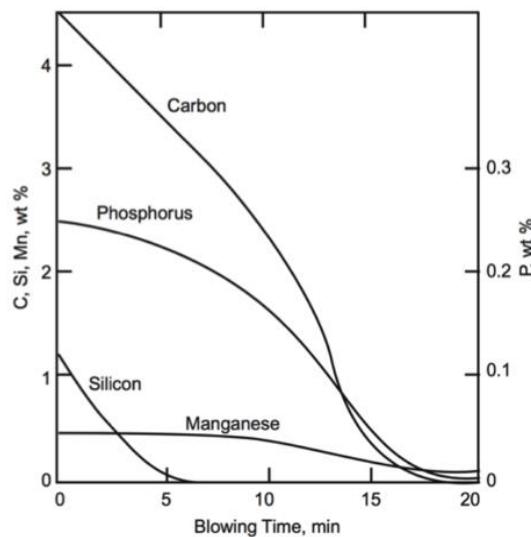


Fig. 5. Graph showing the changes in metal bath composition during oxygen blowing (reproduced with permission from Singh, 2012).

The removal of silicon (Eq. 16 and 17) occurs early in the blowing process (Fig. 5). Similar reactions occur to manganese (Eq. 18 and 19); however, the time profile for the manganese reaction can be attributed to the rising temperature and the variable slag composition (Fig. 5).



The reaction of phosphorus (Eq. 20) is very sensitive to the conditions in the metal bath. During the blowing period 12-25% of dissolved sulfur is directly oxidized (Eq. 21), but desulphurization is slow because it is controlled by diffusion. Part of the sulfur is removed near the beginning of the process when the temperature is still low due to its reaction with manganese, Eq. 22.



The chemical composition of the metal produced determined by sampling from molten metal near the end of the blowing cycle. Once the desired composition is reached, the lance is removed and the molten steel is poured into a ladle. If required, alloying elements can be added to the molten steel. The steel is then poured into ingot molds or into a continuous casting plant, and the slag is poured into a separate ladle and cooled by natural air-cooling, water spraying, water quenching, air quenching or shallow box chilling.

As large amounts of oxygen have been blown into the steel bath, there is often excess oxygen in the steel. To deoxidize the steel, materials are added that have

a high affinity for oxygen, including: manganese, silicon, aluminum, chromium, vanadium, boron and titanium (Peters, 1982). If there is too large a concentration of deoxidizer added there is a risk of the steel deoxidizing (Singh, 2012; Zhang and Chou, 2015).

4. Slag

4.1. Composition and physical properties

The typical chemical composition of basic oxygen steelmaking slag is shown in Table 1 (Shi, 2004). Slag is a mainly non-metallic by-product that is made up of silicates, alumina silicates, calcium aluminum silicates, and iron oxides (Joulazadeh and Joulazadeh, 2010). During the BOS process a proportion of the molten iron cannot be recovered so elemental iron is often observed in the slag (Yildirim and Prezzi, 2011). Slags can be classified into three different categories: ferrous slag (contains iron), non-ferrous slag and incineration slag. The slag often contains a large amount of harmful and heavy metals, so the uses of slag has to be carefully managed to ensure no environmental impact (Shen and Forssberg, 2003). There are also large amounts of phosphorus present in basic oxygen steelmaking slag, which compromises its reuse in steelmaking since the phosphorus content can negatively affect the quality of steel produced (Gautier et al., 2013). The proportions of each element vary from batch to batch, depending on the raw materials and processing conditions (Shi, 2004). Typically, steel slag is non-porous, has a high density and a high crushing strength (Table 2). The variations between individual pieces of slag are clearly shown in Fig. 6.

Table 1

Constituents of steel slag (values sourced from Shi, 2004).

Constituent	Mass(%)
CaO	30-55
SiO ₂	8-20

FeO	10-35
Al ₂ O ₃	1-6
MgO	5-15
MnO	2-8
TiO ₂	0.4-2
S	0.05-0.15
P	0.2-2
Cr	0.1-0.5

Table 2

Physical properties of steelmaking slag (values sourced from Lee, 1974).

Property	
Specific gravity	3.1 to 3.5
Bulk density	1600 – 1760 kg/m ³ (100 – 110 lb/ft ³)
Aggregate crushing value	12 to 25
Aggregate impact value	18 to 24
Aggregate abrasion value	3 to 4
Water adsorption (per cent by mass)	0.2 to 2
Polished stone value	53 to 72

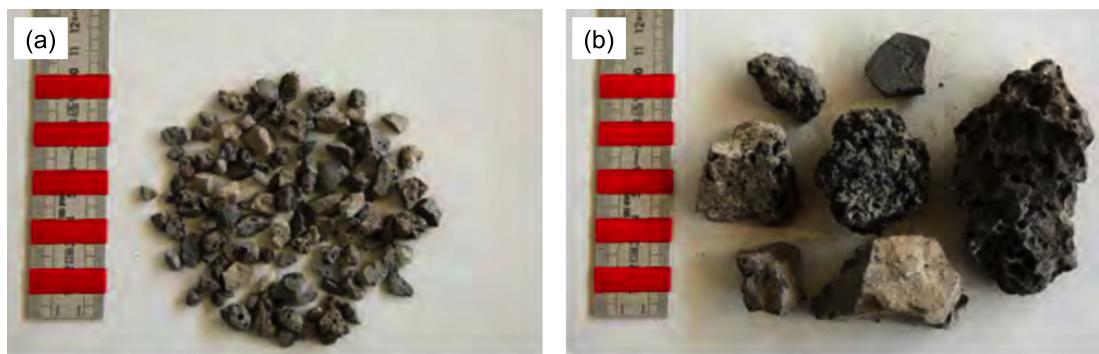


Fig. 6. Image showing the typical physical appearance of BOS slag with sizes in (a) 6-12 mm and (b) 2-5 cm (adapted from Chazarenc et al., 2014).

The presence of calcium silicates in BOS slag such as dicalcium silicate (Ca_2SiO_4 , C_2S), tricalcium silicate (Ca_3SiO_5 , C_3S), and wollastonite (CaSiO_3) induces BOS slag to have cementitious properties (Shi, 2004). In slag characterization *basicity* refers to the ratio of CaO to SiO_2 in a slag sample (Řeháčková et al., 2015). The higher the amount of CaO there is then the higher the basicity of the sample will be. As the basicity of a slag sample increase the cementitious properties of that slag sample will also increase. When in a liquid form a higher basicity can increase the viscosity of slag (Řeháčková et al., 2015).

Both BOS and EAF slag may contain anywhere from 10-40wt% as metal iron (excluding iron oxides) (Horii et al., 2013). To remove the metallic iron the slag is crushed to facilitate separation, using rotating magnetic drum process (Alanyali et al., 2006; Ma et al., 2014; Matino et al., 2014; Bölükbaşı and Tufan, 2014). Crushing the slag to a smaller particle size and as well as increasing the distance between the rotating drum and the blade. The way that the slag has been cooled can have an influence on the amount of metallic iron that can be recovered from the slag (Wang et al., 2012). The magnetic separation process and the crushing process are often repeated several times to increase the amount and quality of metallic iron that can be recovered from the process (Horii et al., 2013). There are also additives that can be added to slags (kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), carbon powder, alumina and silica) that reduce the melting temperature and basicity of the slag, improving the amount of iron that can be recovered (Guo et al., 2018).

4.2. Free lime volume instability

Steel slag is stored in large stockpiles outdoors making it vulnerable to the short and long-term hydration of lime and magnesium oxides. This process, known as *free lime volume instability*, means that the reuse of BOS and EAF steelmaking slag is often limited as many potential applications are outside where moisture could easily cause volume expansion (Eq. 23) (Wang et al., 2010). For example, if the slag

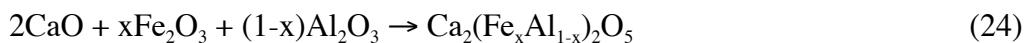
is used in a road surface that gets wet, the free lime expansion can cause the road surface to fracture (Gautier et al., 2013). Basic oxygen steelmaking slag volume expansion has been recorded to be as much as 10% (Mikhail and Turcotte, 1995). At ambient temperature, the reaction proceeds with the formation of the hydroxide (Eq. 23), but $>547\text{ }^{\circ}\text{C}$, dehydration occurs (Wang, Wang and Gao, 2010).



4.3. Free lime volume stabilization

In recent years two methods have been developed to stabilize the free lime in slag and prevent volume expansion: air oxidation or carbothermic reduction.

The first method involves the slag being heated to a temperature of 1673 K under an air atmosphere, and then cooled down to room temperature at a rate of 5 K/minute. When the slag is heated up in air wüstite is oxidized to form hematite, Eq. 13, the latter reacts with the free lime ($\approx 1370\text{ }^{\circ}\text{C}$) and precipitates the mineral brownmillerite ($\text{Ca}_2(\text{Fe}_x\text{Al}_{1-x})_2\text{O}_5$, C_2AF) during solidification (Eq. 24). This method eliminates free lime from the slag, creating many more possibilities for recycling (Liu et al., 2016).



In the second method, the BOS slag undergoes a carbothermic reduction reaction. The Fe and P phases are reduced along with the CaO. Carbon (5-8 wt%), alumina and silica are added to a homogeneous powder of BOS slag. The mixture is then mixed and dried and placed into a furnace at $1600\text{ }^{\circ}\text{C}$ for 1 hour, followed by water quenched (Liu et al., 2017). As the amount of carbon increased the phosphorus-rich phase moved from the slag to the metal. This means that the carbon addition must be kept low to avoid contamination of metallic Fe. The SiO_2 addition stabilizes the free lime and causes C_2S to form, which has cementitious properties,

and its strength gradually increases as it ages. Therefore, the slag can be recycled as some kind of cement product (Liu et al., 2017).

4.4. Leaching behavior of steelmaking slag

With the utilization of steelmaking slags in various applications, there is a risk that the metals contained with the steelmaking slag may begin to leach out causing problems such as water or soil pollution (Shen and Forssberg, 2003).

A study was completed in 2000 in which slag samples were taken from 58 different steel plants in the United States (Proctor et al., 2000). Samples then underwent two separate leaching tests in acidic and neutral conditions. None of the materials that were leached (Table 3) exceeded the safe criterion set out in the Resource, Conservation and Recovery (U.S Environmental Protection Agency, 2006). Since metals are more susceptible to leaching under acidic conditions, the results suggested that it is unlikely that metals would leach out of steelmaking slags under neutral solution. This means slag can generally be categorized as a non-hazardous by-product from the steel industry and could potentially be recycled for use elsewhere.

Table 3

Comparison of slag leachate concentrations from blast furnace (BF), basic oxygen steel (BOS), and electric arc furnace (EAF) slag after leaching at pH 2.8 (values sourced from Proctor et al., 2000).

Element	Criterion	TCLP Leachate Concentration		
		BF	BOS	EAF
Arsenic	5	0.0048	0.0054	0.011
Barium	100	1.2	0.88	1.67
Cadmium	1	0.0054	0.01	0.037
Chromium(VI)	5	0.026	ND	0.018

Chromium (Total)	5	0.22	0.04	1.0
Lead	5	ND	0.015	0.063
Mercury	0.2	ND	0.0005	0.00089
Selenium	1	ND	ND	0.0073
Silver	5	ND	0.029	0.027

5. Land applications

If oils and greases can be removed (and zinc where appropriate) then the slag could be used as a source of iron ore replacement, with the advantages of lowering mining and transportation, both of which contribute significantly to the overall carbon footprint of steel production. However, re-use in steel production is limited at present, but for many years steelmaking slags have been utilized and recycled in the civil engineering industry as cement, roadbed material, aggregate in concrete and in the stabilization of riverbanks (Motz and Geiseler, 2001).

5.1. Concrete

In the production of concrete, aggregate makes up about 70% of what is added into the cement mix. Traditionally natural sand has been used to make up the aggregate in cement, but it is dredged up from riverbeds, which can be damaging to the environment (Takahashi and Yabuta, 2002). In the 1980s scientists began to consider recycling waste materials to replace aggregate in concrete. Testing whether or not cementitious and pozzolanic by-products such as fly ash, granulated BF slag and condensed silica fume could be added as aggregate to create concrete (Lupu et al., 2006; Lupu et al., 2007; Wu et al., 2010). The addition of BF slag as aggregate to cement matched the strength of cement with natural sand as aggregate. In some cases, the BF slag cement was stronger than the natural sand cement (Mehta, 1989).

The replacement of coarse and fine aggregates with steelmaking slag found that the optimum percentage of fine and coarse aggregate was 40% and 30%, respectively (Subathra et al., 2014). The type of steelmaking slag is not specified in

the paper. Higher levels resulted in tensile strength declined. The strength of the resultant concrete is shown for the optimum loadings in Fig. 7. The fine aggregate replacement had significantly better acid resistance comparable to that of conventional cement; however, the concrete created was much less workable than the coarse aggregate concrete (Subathra et al., 2014).

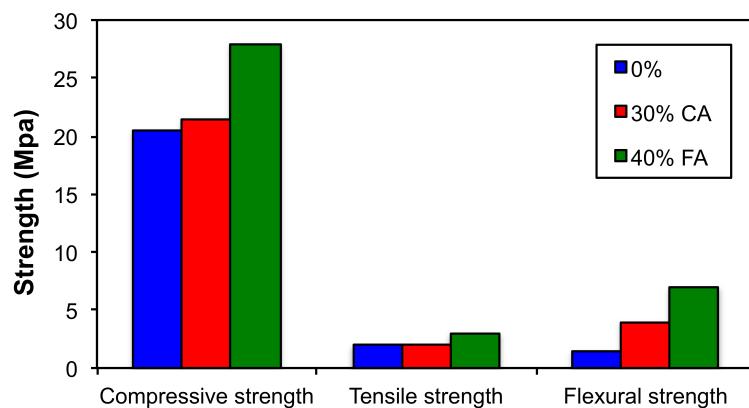


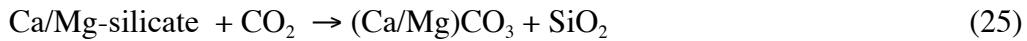
Fig. 7. Figure showing the compressive, tensile and flexural strength of concrete after 28 days made with optimum amounts of course aggregate (CA) and fine aggregate (FA) compared to sand (values sourced from Subathra et al., 2014).

A similar study looked at the influence of adding BOS slag instead of BF slag (Carvalho et al., 2017), although BF slag was still included. It was observed that initially after a period of 28 days the mechanical strength increased (25%), however, after 91 days, the mechanical strength gain decreased (5%). The free lime volume instability in the BOS slag did not appear to be a problem. The use of BOS slag also has economic and environmental benefits. Therefore the replacement of BF slag as aggregate is a viable option (Carvalho et al., 2017).

5.2. Carbon dioxide sequestration

As early as 1995 industrial alkaline residues, including BOS slag, have been exposed to CO₂ to undergo carbonation, as a form of CO₂ sequestration. In the case

of BOS slag, the CO₂ reacts rapidly with the calcium and magnesium silicates (Eq. 25) making it a good option for CO₂ sequestration. In the same process, iron carbonates can also form, however this may not be desirable as the iron may be of better use removed as metallic iron (Huijgen and Comans, 2005).



It has been found that the maximum uptake of CO₂ by BOS slag occurs at 830-850 °C under 1 atm CO₂ (Santos et al., 2012). In addition, BOS slag samples with more free lime absorbed more CO₂, as shown for ‘BOS (II)’ versus ‘BOS (I)’ in Fig. 8. The carbonation of the slag caused the amount of vanadium and chromium leaching to increase, but this heavy metal leaching could merely be suppressed by using the carbonated steel slag as fine aggregate in concrete where the matrix surrounding the slag could act as a sink for any mobile metals (Santos et al., 2012).

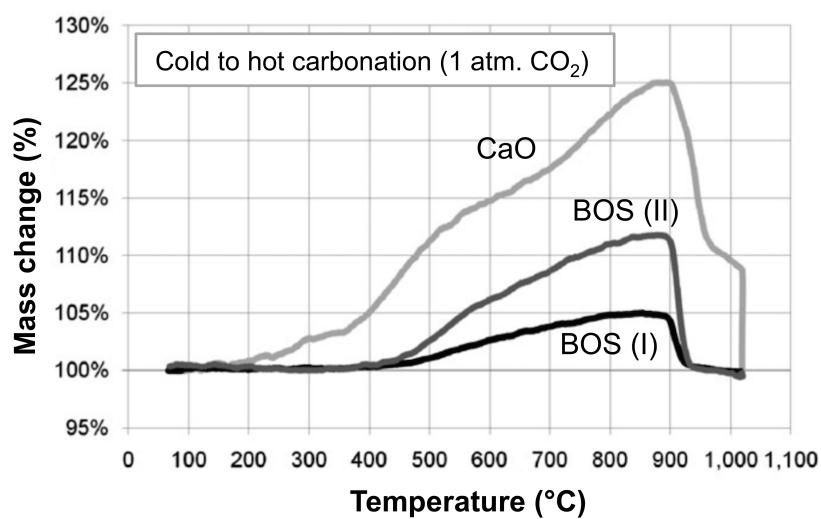


Fig. 8. Graph showing thermogravimetric analysis of BOS slag exposed 1 atm. CO₂ as a function of temperature (adapted from Santos et al., 2012).

One of the issues with the use of BOS slag for CO₂ sequestration is the question as to whether it would simply end up as a waste product, albeit while

storing CO₂ (Sipilä, Teir and Zevenhoven, 2008). Thus, the use of carbonated BOS slag has been investigated as a replacement of aggregate (Pang et al., 2015). Comparing carbonated steel slag aggregate (CSA), un-carbonated steel slag aggregate (SSA), and natural aggregate (NA), the CSA concrete absorbed 5.27 times more water than the NA concrete, and 2.69 times more than the SSA, without affecting the workability of the concrete. After 28 days the compressive strength of the CSA concrete was 20% stronger than the NA concrete and 60% stronger than the strength of the SSA concrete. It was also found that the size and shape of the CSA particles enhanced the compressive strength of the concrete (Scrivener, Crumbie and Laugesen, 2004). A steam test assessing the volumetric stability of the samples, found within 48 hours the SSA concrete cracked and fractured whereas after a period of 240 hours the CSA concrete did not break or show any signs of volume instability (Pang et al., 2015). These results indicated that CSA would be a suitable and cost-effective replacement for natural aggregate as well as being able to store CO₂.

Accelerated carbonation of BOS slag (<10 min.) is possible using a rotating packed bed to accelerate carbonation with lower energy consumption, known as the high gravity carbonation method (Chang et al., 2012). The BOS slag thus produced can be utilized as aggregate in concrete. It was found that up to 0.2 kg of CO₂ could be stored per kg of BOS slag at 30 °C (Chen et al., 2016). It was also shown that when Portland cement is blended with 10% carbonated BOS slag the setting time of the concrete is significantly shortened. The addition of carbonated BOS slag also accelerates the rate at which mechanical strength is gained as the concrete sets. In terms of cost, it was shown that the process would be profitable as the income from capturing CO₂ would exceed the cost of operating high-gravity carbonation (Chen et al., 2016). There is an inverse relationship between particle size and CO₂ uptake (Bodor et al., 2016). Particle size also has a significant bearing on the consistency of the fresh cement: influencing the compressive strength when the cement has set as concrete.

In light of all the above results, CO₂ sequestration for the valorization of BOS slag seems like a realistic solution to many of the environmental problems caused by the steelmaking process. A lot more long-term testing is required before this method can become commercially available.

5.3 Fertilizer

Since the 1950s BOS slag has been used in Germany as fertilizer for crops. The slag caused the crops to grow in larger quantities, without causing any adverse effects in the soil in the short term. Although in long-term studies increased levels of vanadium and chromium have been recorded. BOS slag has also shown good use as a liming material when spread over acidic soils to help to raise the pH to a more neutral level (Annunziata Branca et al., 2014).

5.4. Soil stabilization on land

Before 2006 steelmaking slag was only utilized in the form that it cools (i.e., as coarse aggregate) because of the cost in processing into a fine material. Researchers began to look at if the slag could be used as a soil stabilization material because of its successful use as a fertilizer (Jafer et al., 2018). Soil stabilizers are used to enhance the physical properties of soft soils that are not considered very useful due to their low compressive strength. Ordinarily, Portland cement is used as a soil stabilizer; however other alternatives are needed due to the cements many negative impacts on the environment. Investigation of two different soils (both with clay like properties) combined with the three samples of BOS slag was tested with and without the use of an activator (Poh et al., 2006). The activators used were quicklime and sodium metasilicate pentahydrate (Na₂SiO₃.5H₂O), both having the ability to accelerate the setting time and hydration of the pozzolanic agents in the slag. The result of the study was that BOS slag was successful in stabilizing both of the soil samples and there were considerable improvements in the compressive strength of the soils. But it was shown that a large percentage of the slags used

required an extended curing period to be able to reach these properties, due to the differing chemical composition of the slags. It was also found that the presence of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ as an activator had the best results, through the creation of soluble silica, which enabled the formation of calcium silicate hydrate (C-S-H) and an insoluble metal silicate, which formed the bonding between the fines of the slag and the matrix of the soil. Even though the strength development time of the soils was much slower with slag than with Portland cement, it was concluded that there was high potential for the use of BOS slag in soil stabilization (Poh et al., 2006).

Slag soil stabilization technology has also been utilized in natural disasters such as tsunamis (Gao and Kitamura, 2015). In 2011 the Tokoku earthquake in Japan triggered an enormous tsunami that left behind 13-28 million tons of debris. After the debris was cleared, the soil was ruined for rice production that is so essential to the economy of the area. As the tsunami bought in a large amount of seawater, the soil was saturated with sodium, and the calcium content was much lower than typical. These changes meant that the electrical conductivity of the soil dramatically increased, and the way the soil drained was disrupted, preventing rice being grown. The soil was also highly acidic meaning the ground was high in hydrogen sulfide (H_2S). It was recommended by the Japanese government that steelmaking slag, both BOS and EAF could be used to rectify these problems, since the slag would provide an adequate supply of Ca, Si and Fe. The addition of the calcium ions encouraged the sodium ions to be exchanged from the surface of the soil particles (Fig. 9). The sodium ions were then washed away by rainfall. The iron addition meant that the H_2S was converted to stable ferrous sulfide (FeS). Due to the slags high alkalinity the soil was also de-acidified (Gao and Kitamura, 2015). In Italy in a 2017 study soils that had been affected by excess sodium underwent remediation through the application of BOS slag to the soil (Pistocchi et al., 2017).

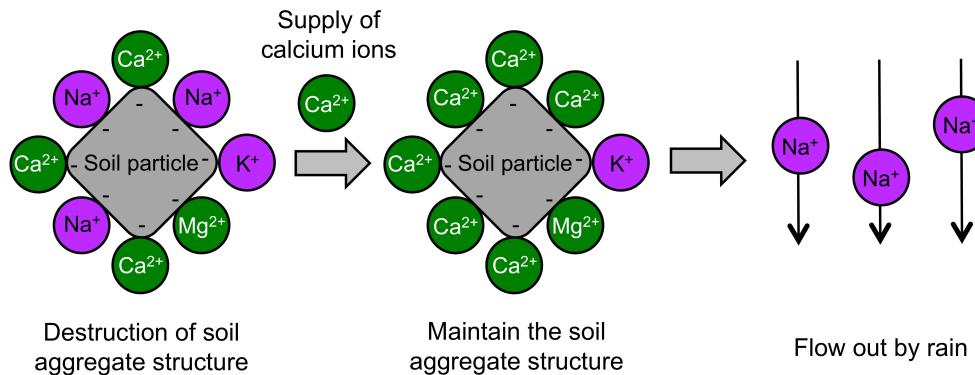


Fig. 9. Flow diagram showing the ion exchange that takes place on the surface of the soil particle between alkali metal (violet) and alkaline earth metals (green) (adapted from Gao and Kitamura, 2015).

5.5 Slag wool

As early as the 1840s slag wool has been manufactured in Wales from steelmaking by-products. The process of making slag wool involves melting the slag and drawing it through a tap hole. The slag then passes through a jet of air, which disperses the slag into a cone of liquid droplets, which then develop into long fibers. The long fibers are then placed into a chamber to dry where small additions of limestone and silica may be added to enhance the properties. Slag wool is often used as insulation in houses due to its good density and insulation properties. Slag wool is resistant to attack from pests, oxidation and is entirely incombustible. All of these properties mean it is extremely suitable to be used as home insulation. In the 1970s slag wool was one of the most significant uses of slag (Lee, 1974).

6. Marine applications

Steelmaking slag is also potentially beneficial to the marine environment due to its high porosity and large surface area. For this reason research into the marine applications of steelmaking slag has increased significantly over the past few years (Yi et al., 2012).

6.1 Restoration of coral reefs

Coral reefs are the most complex and diverse ecosystems on the planet with the number of different species that they can support (i.e., twice as many basic forms of life than all dry land ecosystems combined). This rich biodiversity makes coral reefs essential to the evolution of biological diversity. They also provide significant economic value to humans, especially in developing countries where ecotourism is critical to their economy. In spite of this over one half of the world's population now live in coastal areas having an extremely adverse effects, including: climate change, overfishing, coastal deforestation and pollution.

Coral bleaching has become a significant issue directly caused by climate change. In recent years coral reefs have been subjected to sea temperature rise. When the sea temperature rises above 30 °C for an extended period, the coral begins to expel its symbiotic algae and starts to bleach, losing its color and turning white (Fig. 10) (Glynn, 1993). If this occurs for a prolonged amount of time it kills the coral (Carleton Ray and McCormick-Ray, 2014). In recent years coral bleaching has worsened until 2016 when it was found that 80% of the Great Barrier Reef in Australia had been bleached. There is an extensive research effort going into what would be the most environmentally friendly way to restore coral reefs and the ecosystems surrounding them. Coral reefs are a highly porous material made up of CaCO_3 , similarly, the surface of steelmaking slag is also highly porous and made up of CaCO_3 ; therefore steelmaking slag makes a very suitable artificial reef material.



Fig. 10. Image showing the effects of coral reef bleaching on the Sesoko Island fringing reef (reproduced with permission from Glynn, 1993).

In testing the potential of using slag to create coral reefs, slag cubes (25 cm in diameter) were placed on the sea floor in an inland sea area in Hiroshima prefecture (Takahashi and Yabuta, 2002). After 3 months it was seen that that marine plants and shellfish had begun to colonize the surface of the slag and were growing (Fig. 11) (Takahashi and Yabuta, 2002). Around the bottom of the slag blocks, the same green marine plants were also growing, suggesting that the slag block was having a positive effect on the surrounding environment.

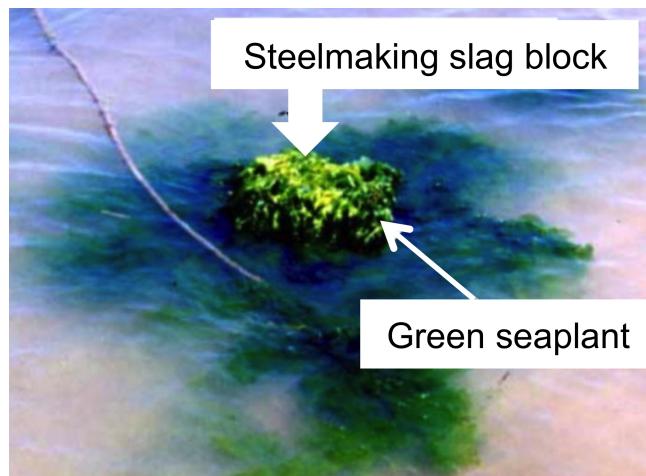


Fig. 11. Photograph of the carbonated BOS block artificial reef with green marine plants and *Zostera marina* seagrass (adapted from Takahashi and Yabuta, 2002).

A comparison between a carbonated slag block, a granite block and a concrete block of the same size, placed in the same area on the ocean floor, and monitored for 9 months. Sargassum plants, a type of seaweed began growing on all of the blocks, however, the highest number of marine organisms was found to be growing on the carbonated steelmaking slag block, see Fig. 12 (Takahashi and Yabuta, 2002). The slag block was the most porous of the materials and hence bears a strong resemblance to the surface of a natural coral reef. The slag block surface was significantly rougher (328 µm) than the granite (67 µm) and concrete (273 µm), which, gave the embryos of the sargassum plants (100-300 µm) a larger surface cavity to live in, which they prefer, explaining the higher number of marine organisms (Fig. 12). The slag blocks are also not high in alkalinity, which was a favorable condition for the Sargassum plants (Takahashi and Yabuta, 2002).

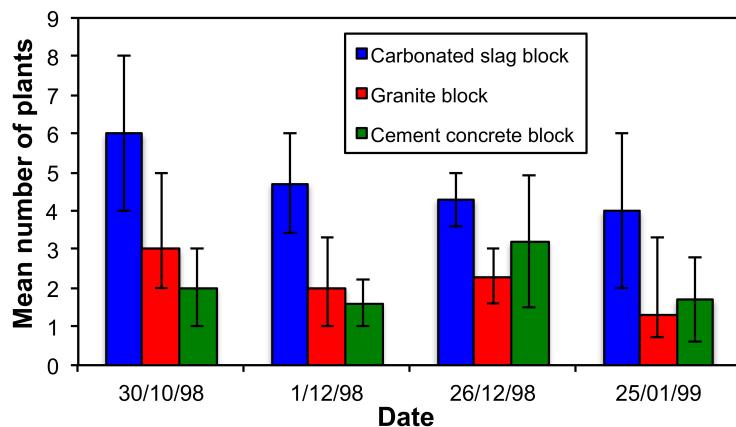


Fig. 12. Graph showing the mean number of Sargassum plants on carbonated slag, granite and concrete blocks as a function of date (values sourced from Takahashi and Yabuta, 2002).

In a subsequent experiment 15 blocks of carbonated steelmaking slag were arranged into a pyramid shape and placed on the ocean floor (Takahashi and Yabuta, 2002). It was discovered that marine plants began to grow in the gaps in between the blocks and in turn this encouraged shoals of fish to start to reside there. This was a

very positive result as many shoals of fish have been driven from the area due to sediment dredging in the area. There were also additional benefits from the pyramid of slag blocks in that effects of sand capping were seen in which nutrient salts were prevented from leaching out and affecting the environment (Takahashi and Yabuta, 2002).

Subsequent to the work in Japan least 40 countries around the world have now adopted artificial reef technology. North America and Australia have begun to use their artificial reefs for recreational use such as diving and fishing meaning their natural reefs cannot get as damaged (Shokry and Ammar, 2009). In an effort to determine whether it is possible to transplant damaged coral species from an unhealthy environment to a healthy environment through the use of EAF slag, several different coral species such as Acroporiidae (*Acropora*), Pocilliporiidae (*Stylophora*) and Faviidae (*Favia* and *Favites*) were collected from damaged reefs. The coral samples were then transported to another location. The samples of slag used in this experiment were not carbonated into blocks, but of irregular shapes and sizes and were collected directly from the steel plant after being cooled. The coral species were fixed to the slag using a small amount of epoxy and seawater cement. After 3 months a thin layer of CaCO_3 began to form over the slag caused by the reaction between the CO_2 in the surrounding seawater and the CaO in the slag. It was found that 70.18% of the 550 coral reef species survived suggesting that EAF slag is a suitable rehabilitation medium for coral reefs in polluted or damaged areas (Mohammed et al., 2012).

Further development of the technology involves an adapted artificial coral reef technology has been created. Granulated BF slag, BOS slag, cement clinker, flue gas desulfurization (FGD), fine and coarse aggregate made of granulated BOS slag and water are mixed to create what is known as a green artificial reef concrete (GARC) (Huang et al., 2016). The concrete was then molded into a cube (100 mm^3) and were then left to set for 24 hours and then cured for 28 days at $20 \pm 2^\circ\text{C}$ under $90 \pm 2\%$ humidity. Nine specimens were placed into the sea for 8 months, near a

naturally occurring coral reef. The density of the GARC (2765.6 kg/m^3) was higher than normal Portland concrete (2400 kg/m^3); the higher density is particularly advantageous as it means that the concrete is more resistant to sea wave action and storms. The GARC also showed an excellent compressive strength (71.4 MPa) and after curing in artificial seawater (92.5 MPa); the increase shows that the artificial seawater worked well with the GARC. After 8 months testing in the sea algae had colonized the entire surface of the specimens. This was a positive result because if barnacles had begun to grow on the surface then it would mean that the GARC had a high pH value. Lower pH value artificial reef materials are known to more easily attract shoals of fish and other marine organisms (Huang et al., 2016). All of the results of this research were very promising however the long-term effects of artificial reefs still require a considerable amount of research. For example, it is unknown how artificial reefs would affect marine communities and food chains (Lee et al., 2018).

6.2. Regeneration of seaweed

Over the past 30 years, the amount of seaweed surrounding Japan's coastline has decreased by 40% due to sea desertification, which is thought to be a direct cause of climate change, rising sea temperatures, overgrazing by sea urchins and changing ocean currents. However, it has also been thought it could be caused by changing mineral levels in the sea such as a decline in the concentration of iron. In light of this, a fertilizer consisting of BOS slag and humus soil was developed by the Nippon Steel Company in Japan (Uemura, 2015). The choice of slag was dictated by its high divalent iron concentration. The fertilizer performed well in the town of Mashike in Hokkaido when it was bought by the fishing cooperative there. It was embedded into the seabed in October 2004 and studied until June 2005, during this time it was found that there was more than 100 times more kelp in the experimental area than there was located in the non-experimental area. The growth of the seaweed has also encouraged fish to come to the area as the seaweed provides not only a food source,

but a place for them to live and procreate. At present kelp and other seaweed species can still be found to be growing very healthily in the area. Several other coastal towns around Japan have now introduced the same technology. Laboratory experiments concluded that it was highly likely the iron eluted from the slag caused the growth of the seaweed (Fujimoto et al., 2012).

Since seaweed has the ability to absorb CO₂ through photosynthesis it is possible that slag can be additionally used to curb climate change (Uemura, 2015). The 40% decrease in seaweed surrounding the coast of Japan, was estimated to have lost the absorption of 7,300,000 tons of CO₂ per year. Thus, a project was initiated with the aim of growing seaweed for the sole purpose of CO₂ sequestration. Carbonated blocks of slag were created (sequestering additional CO₂) and then placed in an experimental area of sea (Uemura, 2015). After 2 months seawater samples were taken and it was found that there was dissolved iron in the water (Uemura, 2015). After 4-6 months it was found that kelp and other seaweed species had settled on the blocks. In this time the seaweed was also sequestering CO₂ in its photosynthesis process. The seaweed was then tested to see if it could be used as a source of biofuel. Only samples of seaweed known as thalli (a green shoot) were collected which were parts of the seaweed that had broken off and were floating through the water. The thalli was successfully converted into oil or resin, although it is also not known how well the oil produced would perform in an industrial oil application; however, it has been reported that different seaweed species produced different amounts of biomethane (Tabassum et al., 2018) suggesting a promising application.

6.3. Phytoplankton application

An innovative marine application of steelmaking slag has been its use for elution of iron-ions to stimulate Phytoplankton to absorb CO₂ (Futatsuka et al., 2004). Phytoplankton are microscopic organisms that are an essential component of ecosystems in oceans around the world, which can sequester 2 kg/m².year of carbon,

making them useful in the reduction of carbon (Futatsuka et al., 2004). Certain types of phytoplankton, specifically diatoms, grow fastest in the presence of iron, silicon, phosphorus and nitrogen, which could be sourced from steelmaking slag (Nakamura et al., 1998). Thus, the use of slag as a nutrient resource using seawater taken from Sendai Port in Japan showed a positive effect on the growth of marine phytoplankton (Haraguchi, Suzuki and Taniguchi, 2003). However, a concentration of >330 mg/L resulted in growth inhibition due to an extreme pH increase (Haraguchi, Suzuki and Taniguchi, 2003). Similar experiments have been reported (Yamamoto et al., 2016) and there are various studies on how phytoplankton could be used as biofuel (Tabassum, et al., 2018).

6.4. Sand capping

Overfishing and waste products leaching consequences have had extremely harmful effects on coastal ecosystems around the French Riviera (Carleton Ray and McCormick-Ray, 2014). In the 1980s 8000 m³ of artificial reefs created of waste rubber tires were deployed to try and remediate the effects of the steadily increasing coastal population (Risso-de Faverney et al., 2010). The artificial reefs intended purpose was to restore the coastal ecosystems, however, they had the opposite effect (Collins et al., 1995).

It is observed that high amounts of zinc were detected leaching into the sea. It was estimated that 10 mg per tire leached out every 3 months (Collins et al., 1995). This was inline with the previous observation that mussels growing on an artificial tire reef in the French Riviera did not develop as well as those growing in a separate location not in the presence of rubber tires (Risso-de Faverney et al., 2010). To avoid further pollution the French Government would like to remove the tires, unfortunately, the effects that this would have on the environment are unknown, as the sediment left behind would be polluted. In the past to remove polluted sediment methods such as dredging have been used but this is costly and can lead to secondary pollution, as well as disruption of the ecosystem. In a pilot scheme at Université de

Nice Sophia Antipolis the potential of using steelmaking slag to cap the contaminated sediment has been initiated.

Previously activated carbon (AC) has been used to cap contaminated soils in oceans. But the cost of AC has significantly risen in the past few years, making steelmaking slag a suitable replacement. Steelmaking slag and bauxaline (a by-product of creating aluminum products) were chosen as candidates as they are both low cost by-products from industrial processes. Sediment samples, polluted with cadmium, zinc, arsenic and chromium, were collected from the sites at which the tires were located. A 1-1.5 cm layer of the steel slag, bauxaline and a mixture of both were applied to the artificial polluted sediment; uncapped sediment was also assessed (Taneez et al., 2018). The samples were then topped with an unpolluted artificial seawater solution and an aliquot collected weekly. The concentration of each element was assessed, and both of the capping materials performed well yet steelmaking slag was the only material that was capable of capturing Cr; however, the steel slag did cause highly alkaline conditions in the sediment, the pH of the seawater to 12.3. It was concluded that it might be better to use a mixture of bauxaline and slag, as this would create a more neutral pH environment (Taneez et al., 2018).

6.5. Sand alternatives

In some areas around the world such as in coastal regions of Japan soft clayey soils are found, caused by dredging (Juneja, 2015). To improve stability a process called sand compaction piling involves injecting sand into the ground to a predetermined depth. The sand forms a column and forces the surrounding clay material to become a lot more compacted and stronger (Juneja, 2015). An alternative to sand would be BOS slag, and initial studies have shown that the slag did not cause a drastic pH increase in the surrounding sea (Horii et al., 2013). Before being compacted into the ground, the slag was stabilized by carbonation, or the slag was mixed with some of the clay-like soil from the area that had been dredged. Steelmaking slag is characterized as being high in calcium; therefore, calcium ions

are often eluted from the slag, which have the ability to lower the phosphorus content of the water by absorbing part of the insoluble phosphorus. The sulfate concentration is also reduced by the elusion of the calcium ions, therefore, preventing the formation of hydrogen sulfide, which can have detrimental effects on marine organisms. As steelmaking processes vary day to day the by-products produced may also vary, so the slag must undergo a leaching test to check for any heavy metal leaching before it can be used as a sand alternative. In light of these results, many ports in Japan began to use steelmaking slag to improve the soil in their ports with excellent results and no adverse effects (Horii et al., 2013).

6.6. Hydrogen sulfide removal

An increase in hydrogen sulfide in oceans is a direct effect of the effects of dredging to make sure that boats have enough depth to be able to navigate in waters close to harbors. The process causes sludge to form on the bottom of the dredged area, and H₂S is produced from the degeneration of the biological environment under decreased oxygen concentrations (Hayashi et al., 2013). Areas that have been dredged are often refilled with natural materials such as sand or crushed stone. BOS slag has been shown to be more effective at the suppression of H₂S than natural materials (Hayashi et al., 2013). It was also found that the sludge in contact with the slag had a lower sulfide concentration, and a higher concentration of oxygen in the sludge, reducing H₂S generation. X-ray absorption near edge structure (XANES) analysis showed that the mechanism of H₂S removal involved the formation of iron and manganese sulfides and the precipitation of sulfur by oxidation. Fe(OH)₃, and not FeS₂, was identified as the major iron species formed on the slag at the end of the experiment suggesting that iron cannot play an important role in the removal of H₂S. The content of MnS was found to increase significantly at the end of the experiment (19%), the remaining sulfur (81%) was found to be in its elemental form. MnS is thermodynamically unstable it can be assumed that the MnS is oxidized to become elemental sulfur. In seawater, it has been observed that the oxidation of

sulfides occurs via manganese oxide, Eq. 26 (Kim et al., 2012).



The difference was between adding steelmaking slag, FeO, or metallic iron to artificial seawater on sulfides has been investigated (Hayashi et al., 2014). In the case of slag, Fe in the slag reacted with the sulfide irons to form sulfides of iron, known as troilite (FeS) and pyrite (FeS₂). There was a shift to an oxidizing atmosphere, which caused sulfide ions (S²⁻) to form sulfate ions (SO₄²⁻) (Hayashi et al., 2014). These are in agreement with studies in which it was seen that the H₂S reduction mechanisms were the oxidation of sulfur by the reduction of manganese oxide and the formation of pyrite (Asaoka et al., 2013).

Field experiments have been undertaken in Fukuyama Harbor that has had problems with residents noticing an odor caused by H₂S throughout the spring to summer (Miyata et al., 2018). Blocks made of slag known as “Marine Stone™” were placed onto the sea floor in the areas where the odor was a problem, and the water and sediment quality were assessed as well as the gases produced by the area. Over a 2-year period it was observed that the amount of dissolved sulfide was dramatically reduced and the amount of oxygen in the water increased, importantly, the odor emitted by the sea was also significantly reduced (Miyata et al., 2018).

6.7 Metalloid removal from wastewater

Hexavalent chromium (Cr(VI)) salts are used extensively in industry as it provides absolute protection against corrosion (Thuy et al., 2016). It has been found to be toxic so is being banned under REACH legislation from the year 2019 (Montemor, 2014); however, it has already leached into wastewater and given its carcinogenic nature there is a need to remove Cr(VI) from wastewater to prevent further harm. Studies of the interaction of Cr(VI) with slag has shown that the mechanism of removal involves release of Fe²⁺ (Fig. 13), which leads to the

reduction of Cr(VI) to not toxic trivalent chromium (Cr^{3+}) and concomitant formation of Fe^{3+} (Park et al., 2008; Han et al., 2016). These results were very promising for the problem of hexavalent chromium wastewaters.

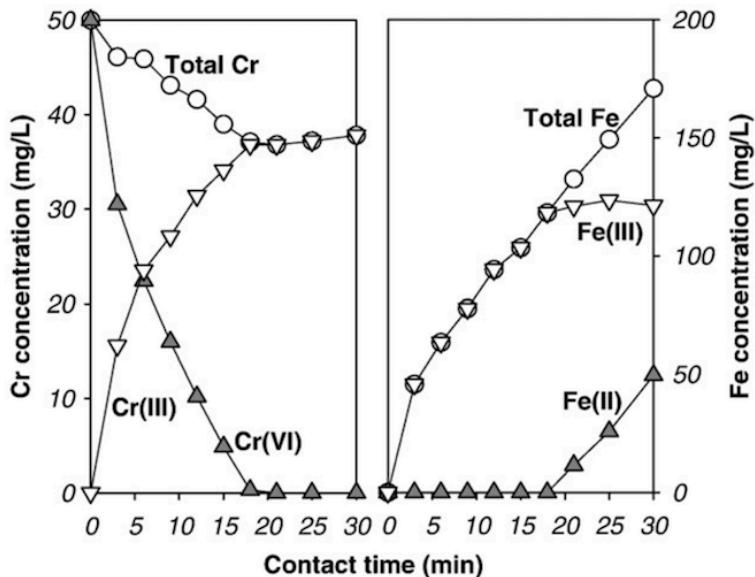


Fig. 13. Graph showing the removal dynamics of 50 mg/L of Cr(VI) by 5 g/L waste slag, consisting of Fe(II) and Fe(III) (reproduced with permission from Park et al., 2008).

Arsenic is extremely toxic to humans (Gomez-Caminero et al., 2001), and the World Health Organization has stated that the safe limit for arsenic in drinking water is 0.01 mg/L, as a consequence many countries have implemented technology to remove arsenic (Mohan and Pittman, 2007). It has been shown that one of the optimum ways to remove arsenic is to use steelmaking slag. As shown in Fig. 14, slag can eliminate 90% arsenic from a solution concentrated at 1.25 g/L in 2 hours (Chakraborty et al., 2014). Arsenic removal is more efficient in alkaline solutions. In acidic solutions, silica and phosphate leach more than iron meaning arsenic removal is hindered. At higher pH calcium leaches out to form $\text{Ca}(\text{CO}_3)$, which helps to remove arsenic by co-precipitation (Chakraborty et al., 2014).

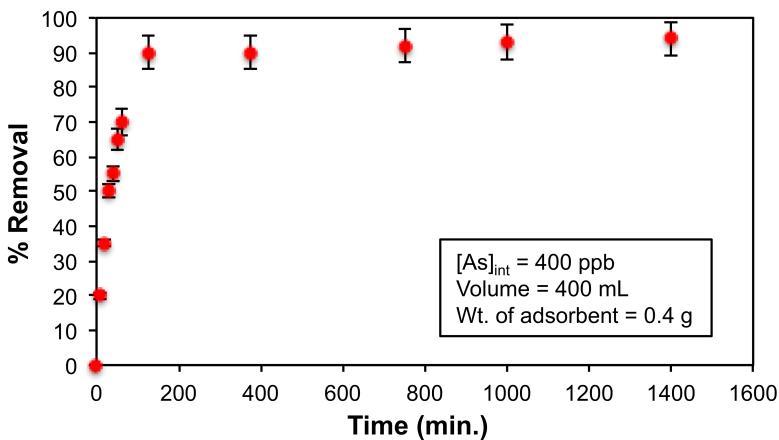


Fig. 14. Graph showing the rate at which steelmaking slag removes arsenic from water (values sourced from Chakraborty et al., 2014).

6.8 Phosphorus removal from wastewater

Phosphorus is a common nutrient that is found in water, but surface runoff from sewage treatment works, and the use of phosphorus in fertilizers is one of the biggest causes of phosphorus pollution in surface water. High amounts of phosphorus can lead to eutrophication (an excessive amount of nutrients), which causes a layer of algae to form on the surface of the water, preventing any exchange of gases between the atmosphere and the water, meaning that all plant and marine life deteriorates in the body of water (Mortimer, 1971; Fillos and Molof, 1972). As the adsorption capability of calcite (Freeman and Rowell, 1981) and magnesium silicate (Smith and Mine-Yun, 1978) is good, researchers tested whether steelmaking slag could be used in a similar application since it contains both calcite and magnesium silicate (Yamada et al., 1986). Assessing the influence of pH, NaCl concentration and the surface characteristics of the slag in the research, the optimal pH for the adsorption of phosphorus onto slag was found to be pH 8, with slags that had a larger pore size.

Between 1990 and 2015, the average orthophosphate (PO_4^{3-}) concentration found in European rivers and lakes has been reduced to 0.05 mg P/L (from 0.12 mg P/L) and 0.027 mg P/L (from 0.04 mg P/L), respectively (European Environment

Agency, 2015). The decrease is due to less phosphorus being used in detergents as well as wastewater outlets being diverted away from rivers and lakes. In spite of this effort, there is still a problem with phosphorus runoff from fertilisers used in farming. The EU framework directive stated that all member countries must achieve good water quality status by 2013. In light of these demands BOS slag has been tested to see if it could be used (Bowden et al., 2009). The slag was placed in a flow through reactor for the experiment. The initial phosphorus concentrations reflected values that had been recorded in the real world in agriculture. The experiments ran for a total of 406 days and showed that the maximum amount of P removal was 62% (Bowden et al., 2009).

EAF and BOS slag were compared in a 2-years field experiment in an area of constructed wetland, which had a high concentration of phosphorus in its effluent (Barca et al., 2013). It was observed that the EAF slag filter only removed 37% of the total phosphorus whereas the BOS slag filter removed 62%. Calcium slag dissolution and calcium phosphate precipitation were the two mechanisms of phosphorus removal observed (Bowden et al., 2009; Blanco et al., 2015). The pH of the filtered wastewater was elevated during the first 5 weeks of the experiment and then stabilized to below pH 9.

Several methods are currently being investigated to optimize phosphorus removal. First, the combination of BOS slag and bacterium *Alteromonas* 552-1 performed well to remove 90% phosphorus at pH 7.8-8.0 (Zhou et al., 2016). Second, applying a NaOH coating to the slag was meant to allow a higher pH to be maintained for a longer period, unfortunately, it was still compromised with its exposure to aqueous solution (Park et al., 2017).

7. Carbstone Process

The transformation of steelmaking slag into a strong structural material through high gravity carbonation (Chang et al., 2012). Now known as the *carbstone* method (Quaghebeur et al., 2015), it consists of three steps: pre-treatment, shaping

and curing.

The BOS slag is first homogenized into a powder and then mixed with the appropriate amount of water. The amount used in the method being referenced was 10 wt%, but it does depend on the initial moisture content of the slag. The mixture is compacted into the desired shape using a hydraulic press ($75\text{-}609 \text{ kgf/cm}^2$). The shape depends on the desired application of the slag block. The block is then placed into an autoclave at $20\text{-}140^\circ\text{C}$, for 16 hours, with a CO_2 enriched atmosphere at a pressure of 0.5-10 MPa (Quaghebeur et al., 2015). The carbonated block shows excellent compressive strength and environmental properties making it suitable to be used as a construction material. One of the advantages of this process is there is no need for an additional binder (Pang et al., 2015).

The carbstone process has not been tested in a marine environment, but a similar experiment using slag have been conducted using concrete blocks containing different amounts of slag. Located on Treat Island (Maine, USA) is a marine exposure site, which has been used for 75 years to assess the effects that a marine environment has on different kinds of concrete (Thomas, 2016). The site is exposed to the North Atlantic environment, which is a very severe environment with tides up to 6.7 m, chloride concentration of 19.3 g/L, a salinity of 35.2 g/L and approximately 100 freeze-thaw cycles per year. From 1978-1987 various concrete blocks containing slag on Treat Island to be assessed for 25 years (Malhotra and Bremner, 1996). The blocks contained other constituents, but there was a set of concrete blocks that contained different percentages of slag, which were visually assessed. It was found that there was the most significant deterioration on the block with 65% slag after 25 years. The blocks that had lower water/cementitious material (W/CM) ratios deteriorated the least. It was also seen that the resistance to chlorine permeability was significantly increased with the addition of BOS slag. The study highlighted the importance of having a low W/CM ratio when BOS slag is used in concrete (Thomas, 2016). A method has been developed to predict the performance of marine concretes by using numerical modeling and some laboratory-based tests (Nanukuttan

et al., 2015). It has been shown that the data collected from chloride testing can be used to predict the effects of chlorine in any given environmental conditions. The model is an encouraging start to modeling marine concrete behavior although the accuracy of the model for predicting more extended periods in the future still needs to be improved.

8. Conclusions

- The viability of the steelmaking industry being able to continue in the long term can be said to strongly depend on whether the adverse effects caused by the industry can be lessened and the process made much cleaner.
- This depends on how the steel industry can be transformed from a linear economy into a circular economy in which the by-products produced by the industry can be reused.
- The by-products can be used in a way that reduces resources as well as providing added benefits such as CO₂ sequestration.
- Given the critical need of global heavy industry to decarbonize, the re-use of steelmaking slag offers an alternative to both the use of raw materials whose production is environmentally impactful, and the control of existing environmental damage.

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