SMELTER SLAG - SEEKING MARKET OPPORTUNITIES & CARBON CREDITS AND IN A CHANGING WORLD

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ABSTRACT

The profitable marketing of smelter slag in an environmentally acceptable form has been a long-term aim of the copper smelting industry. Successful marketing of copper slag converts a waste into a product. Slag properties are discussed and investigation of potential uses for slag in emerging industries proposed. The scope for a carbon credit is examined. A basis for setting a long-term target market price for slag is postulated. A need to encourage interest in finding new uses for slag is emphasised and a competition to stimulate broadly based proposals is proposed.
CHAPTER 01  Processing of Slags

INTRODUCTION

Non-ferrous smelters are rarely large direct consumers of fossil fuels relying instead on electrical energy, either directly for submerged arc smelting or for production of tonnage oxygen for autogenous smelting of the sulphide feed. The direct use of fossil fuel is therefore limited to the chemical control of oxygen potential usually to minimize slag losses. However to the extent the fossil fuels are used for the production of electricity the associated carbon dioxide emissions may be attributed to the smelting operation. While the improvement in the efficiency of process energy use offers in principle scope for claiming a carbon credit, in practice the options are limited. Direct heat recovery from process gases is only attractive where steam can be beneficially used as in an associated refining operation. Heat recovery from molten slag has been tried [12, 17] but the value of the recovered heat does not appear to justify the additional capital and operating costs whether recovered directly or by delivering the molten slag to an additional operation such as metallic iron or rock wool production. The remaining option is to develop an economically and environmentally acceptable market use for smelter slag. If the product marketed is a granulated product the heat content of the slag can be attributed to the production of the slag product since fusion is an essential preliminary to granulation. This may provide a basis for claiming a carbon credit for reduced energy consumption for the production of copper.

Additionally the granulated slag product itself may justify a carbon credit if it displaces a product that involves higher carbon dioxide emissions. An example is the displacement of fossil fuel intensive cement by granulated iron blast furnace slag with pozzolanic properties. Attempts have been made to liberate the pozzolanic potential of granulated non-ferrous slag thus far with only limited success.

This paper focuses on the search for new applications for granulated non-ferrous slag based on the needs of new technologies and unappreciated properties of slag. The new technologies currently in a state of innovative ferment include solar power generation; more efficient food production; more productive fish farming and contaminated water purification and recycling. While such applications are unlikely to qualify directly for carbon credits, to the extent that the driver behind many of these innovations is to reduce carbon emissions there is an indirect credit in the creation of new markets for granulated fayalite slag.

Some of the properties of granulated slag that suggest potential application in these fields include high and consistent hydraulic and air permeability; high specific gravity; high heat capacity; ability to adsorb solar radiation; and, possibly, surface catalytic potential. Non-ferrous slag is comprised mainly of the mineral fayalite. Fayalite is rarely found in the earth’s crust, which perhaps explains the lack of attention paid in scientific circles to the properties of the product. A search of the literature disclosed that astrophysicists have studied the properties of fayalite dust in space while geo-physicists are interested in the properties of the Earth’s mantle but a study of the solid properties of the only significant concentrated source of fayalite on the Earth’s surface, smelter slag, has attracted little or no scientific attention.

It is suggested that a start be made to fill this knowledge gap on fayalite properties and to evaluate of potential use of granulated smelter slag in new technologies. The smelting industry might consider initially stimulating interest in the subject by offering prizes for proposals that lead to profitable and environmentally acceptable uses for slag.
**BACKGROUND**

This paper is written to stimulate interest in and encourage efforts to examine more closely the properties of granulated copper smelter slag and to explore more broadly the new and rapidly growing opportunities for slag markets arising out innovations to address the global shortages and rising costs of fuel, farm products, fish and fresh water. It is postulated that these challenges will lead to technical developments that will create new, rapidly expanding and profitable opportunities for copper slag sales with emphasis on the granulated product. These uses will be built on the recognition of the value of unique property combinations drawn from a list that includes:

- High specific gravity
- High specific heat
- Consistent size distribution
- Narrow size range
- High hydraulic conductivity
- Thermal stability
- Chemical stability
- Solar absorptivity
- Surface nano-porosity (uncertain).

These properties need to be matched with needs in the new and rapidly growing segments of the economy such as:

- Solar and wind energy systems
- Biomass gas processing
- Hydroponic growing facilities
- Land based fish farming
- Sea defence construction
- Off-shore drill rig stabilization
- Storm water collection, filtration and surge control
- Water storage and conservation
- Daily/seasonal thermal capacitors.

Massive fayalite deposits do not occur in nature. Once markets are established for all available smelter slag the price will be set by the cost of synthesizing granulated slag from natural materials. It is unlikely that the technology of these new emerging uses will be within the field of expertise of the copper smelting industry and developing them will be seen as a diversion from the core business. Expanded knowledge of slag properties and multi-disciplinary cooperation is required to properly evaluate and develop these market opportunities. It is proposed to initiate this project by issuing a web-based challenge to the global scientific - technical - entrepreneurial community to identify and evaluate new slag uses. A suitable reward will be required for proposals submitted that lead to new, profitable and environmentally acceptable product markets above a threshold size. The reward would provide a tangible incentive to study solid slag properties and participate in the competition to build new slag markets. (Viz. Barrick Silver challenge).
METHODOLOGY
The scope of this paper is very broad and draws on knowledge and experience from a decade devoted to gathering available information on slag, undertaking investigative work into slag properties and meetings and discussions with current or potential slag users plus involvement in programs to improve energy efficiency and reduce greenhouse gas emissions.

RESULTS AND DISCUSSION - SLAG MARKETING

Past Record
The status of many past efforts by industry and academia to develop productive uses for copper smelter slags has been well reviewed [3, 7, 9, 16, 18, 21, 22]. It would be redundant to duplicate this work. It is perhaps sufficient to say that sales had been limited by small market size for industrial minerals; high grinding costs for pozzolanic applications; high capital and energy cost for thermal reduction for iron or metal recovery and environmental concerns with dispersive uses such as road grit (winter sand) and railway ballast. Most of these markets are mature and are well supplied by alternative low cost materials. The economic shipping distance to potential users also limits market penetration when plentiful low costs alternatives (such as sand and gravel) are widely available.

Future Scope
New and greater opportunities for marketing copper slag are expected to arise as a result of the interplay of many factors including:

- Improved smelter quality control
- Intensive study of slag properties
- Absence of natural deposits of massive fayalite mineral
- Establishment of an international commodity market for copper slag
- Innovation in response to global shortages of fuel, food and water
- Incentives related to non-carbon sources of energy.

These factors are examined in somewhat greater detail below:

Smelter Quality Control
The quality of copper smelter slag is improving as a result of wider adoption of slag cleaning to remove residual copper [13]. An example of a clean slag analysis is given in Table 1.

Table 1: Example of fayalite slag analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>FeO</th>
<th>SiO2</th>
<th>CaO</th>
<th>Al2O3</th>
<th>MgO</th>
<th>Cu</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis %</td>
<td>49.0</td>
<td>34.5</td>
<td>2.3</td>
<td>3.0</td>
<td>2.0</td>
<td>0.6</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Granulation technology has also improved yielding a more consistent (uniform) size distribution. Different granulation procedures give different median sizes over the range 0.6 to 1.2 millimetre diameter.
**Slag Property Determination**

Smelting operations, the owners of most stockpiled slag, have control of the world supply of commercial fayalite mineral. The operations are generally ambivalent in attitude to marketing slag. On the one side there is a desire to see slag marketed in an environmentally acceptable and profitable way. On the other smelters have been reluctant to invest money in the study of slag properties and the development of new markets that are seen to offer only a modest return at best. Additionally due to the potential for frivolous lawsuits there has been a reluctance to release material for entrepreneurs to market even when the product passes all relevant environmental tests. Where entrepreneurs such as MRRI Tucson Arizona; Green Diamond, Riddle Oregon; Fisher-Wavy Sudbury, Ontario have obtained access to slag supplies, small but profitable businesses have been developed serving a diversity of niche markets. The most common current use of granulated slag is for abrasive cleaning of surfaces and the physical properties of granulated solids related to this use are fairly well documented such as size, specific gravity and hardness. Public information on other properties such as thermal conductivity, radiation adsorptivity, heat capacity, hydraulic conductivity, gas permeability, catalytic activity, chemical reactivity, and packing density is rare to non-existent. Some thermal properties of fayalite are documented in geological papers for the Earth's mantle and in astronomical texts for solar dust but information related to potential terrestrial use is lacking. These gaps need filling in order to fully evaluate slag market potential.

**Fayalite Supply Limitations and Potential Price**

The principal mineral in copper smelter slag is fayalite (Fe$_2$SiO$_4$). Fayalite, while present in dispersed crystals in olivine rock, is seldom if ever found in massive naturally occurring deposits and never in granulated form. While commercial olivine, a mixture of forsterite and fayalite minerals has a composition close to that of the earth's mantle; smelter slag (fayalite) is substantially different in composition and physical properties. A comparison of fayalite analysis with the inferred composition of the Earth's mantle may provide a partial explanation for this dearth of supply since MgO dominates the mantle.

<table>
<thead>
<tr>
<th>% Wt</th>
<th>Earth's Mantle</th>
<th>Cu Slag</th>
<th>Commercial Olivine</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>46</td>
<td>35.0</td>
<td>45-51</td>
</tr>
<tr>
<td>MgO</td>
<td>38</td>
<td>0.8</td>
<td>40-43</td>
</tr>
<tr>
<td>FeO / Fe$_2$O$_3$</td>
<td>7.5</td>
<td>51.0</td>
<td>7-8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.1</td>
<td>3.3</td>
<td>1</td>
</tr>
<tr>
<td>CaO</td>
<td>3.2</td>
<td>3.0</td>
<td>0.2-0.8</td>
</tr>
</tbody>
</table>

Once markets are established for all current quality copper smelter slag production, the price of additional supplies will be determined by the cost of reprocessing historical stockpiles and ultimately undertaking the fusion of iron oxide and silica. An illustrative estimate of the capital and operating cost for a stand alone green fields electric furnace reduction melting operation to produce 1000 t/d of a granulated fayalite slag product by reacting iron ore with silica sand according to the Equation (1):

$$\text{Fe}_2\text{O}_3 + \text{SiO}_2 + \text{C} = \text{Fe}_2\text{SiO}_4 + \text{CO}$$ (1)
CHAPTER 01  Processing of Slags

Is given in Table 3.

Table 3: Illustrative estimate of the cost of producing granulated fayalite slag in a stand alone operation

<table>
<thead>
<tr>
<th>1000 tonne per day operation</th>
<th>US$/t Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand 0.3 t @ US$20/t</td>
<td>6</td>
</tr>
<tr>
<td>Iron Ore 0.8 t @ US$60/t</td>
<td>48</td>
</tr>
<tr>
<td>Carbon Char 0.1 t @ US$200</td>
<td>20</td>
</tr>
<tr>
<td>Power 600 kwh/t @ US$0.05/kwh</td>
<td>30</td>
</tr>
<tr>
<td>Labour 50 people @ $200/day/person</td>
<td>10</td>
</tr>
<tr>
<td>Supplies - operating &amp; maintenance</td>
<td>5</td>
</tr>
<tr>
<td>Total operating</td>
<td>119</td>
</tr>
<tr>
<td>Capital charge on US$36,000,000 @ 20% p.a.</td>
<td>20</td>
</tr>
<tr>
<td>Total Cost</td>
<td>139</td>
</tr>
</tbody>
</table>

Table 2 suggests an eventual floor price for granulated slag of US$100+/tonne.

**Regulatory and Commercial Factors**

Factors expected to open new market opportunities for granulated smelter slag include:

- Rising prices for finite supplies of fossil fuel, food supplies and clean water driven by expanding world population and rising standards of living stimulating the search for innovative ways to provide energy, grow food and purify water;

- Regulatory pressures and incentives to reduce carbon dioxide emissions that may offer direct opportunities for carbon credits; and, more importantly, the incentives for reducing carbon dioxide emissions through alternative energy development, efforts to expand food production using more fuel efficient techniques and to conserve fresh water while purifying and recycling contaminated water in more energy efficient ways;

- The development of a commodity market for granulated slag that is expected to develop facilitating global distribution. [14] once beneficial uses for a significant portion of copper smelter slag production meeting market specification is established.

All of these factors ways are leading to many innovative techniques in which granulated slag may have an important role to play.

**Pertinent Slag Properties & Potential Applications**

The open literature contains very limited information on the properties of copper smelter slag or fayalite mineral. The limited information available suggests that fayalite slag may have a unique and valuable combination of properties for a number of applications that are inadequately documented, publicized and appreciated by the entrepreneurial community. Some examples follow to encourage critical analysis and constructive thinking on the subject by others. Granulated slag with its thermal stability, high heat capacity, high thermal conductivity and gas permeability may also be valuable in storing heat below, as well as above, the fusion temperature of salt. Slag has a high absorptive capacity for solar energy, is chemically stable and has high and consistent hydraulic conductivity/gas permeability. These are all desirable properties for a primary passive solar energy receptor [6].

Quantification of high solar absorptive capacity of granulated smelter slag in scientific-engineering terms is required. Spectral absorption studies have been focused on geological [2, 4] and astronomical interests [20] and are not easy to interpret for practical purposes in surface terrestrial terms.
Table 4: Copper slag properties for solar heating units

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Granulated Copper Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity</td>
<td>Cms/sec</td>
<td>1-10</td>
</tr>
<tr>
<td>Gas permeability</td>
<td>M/sec</td>
<td>1-10</td>
</tr>
<tr>
<td>Size distribution (median)</td>
<td>Microns</td>
<td>600-1200</td>
</tr>
<tr>
<td>Solar absorptive bands</td>
<td>Nm</td>
<td>500/1000</td>
</tr>
</tbody>
</table>

The solar heating of slag appears to be enhanced by the translucency of the slag and iron absorption bands at around 500 and 1000 nanometre wavelength permitting internal heat capture rather than reflection. Figure 1 shows the olivine adsorption bands are within the peak of solar radiation spectrum.

![Solar Radiation Spectrum](image)

The solar heating of slag appears to be enhanced by the translucency of the slag and iron absorption bands at around 500 and 1000 nanometre wavelength permitting internal heat capture rather than reflection. Figure 1 shows the olivine adsorption bands are within the peak of solar radiation spectrum.

The 500 and 1000 nanometre olivine absorption bands are both well within the main distribution range of solar energy at sea level suggesting there could be a role for copper smelter slag in passive solar heating units for domestic or commercial use.

Concentrated solar power (CSP) is attracting increasing attention for generating electricity or process heat in hot desert areas [15, 23]. Molten salt is used as the heat capacitor to permit energy generation to be maintained overnight. Power generation also requires a heat sink and granulated slag may serve this function as well as storing lower grade heat (below the fusion temperature of salt. Passive solar systems are increasingly popular for water and space heating in urban environments. Both require heat storage on a daily basis to smooth out the delivery to the consumer. While water is often the capacitor of choice for residential and commercial buildings, granulated slag may find a role in passive solar systems as a heat capacitor where a dry system is preferred. Copper smelter slag has a high solid heat capacity [1]. It compares favourably with sand, the most obvious low cost alternative, in both these properties.

Table 5: Copper Slag properties with thermal capacitor potential

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Granulated Copper Slag</th>
<th>Commercial Sand</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>Gms/cc</td>
<td>4.2</td>
<td>2.6</td>
<td>1</td>
</tr>
<tr>
<td>Specific heat (Wt)</td>
<td>J/gm/ºC</td>
<td>0.65</td>
<td>0.71</td>
<td>4.2</td>
</tr>
<tr>
<td>Specific heat (Vol)</td>
<td>J/cc/ºC</td>
<td>2.73</td>
<td>1.84</td>
<td>4.2</td>
</tr>
<tr>
<td>Size distribution</td>
<td>Microns</td>
<td>~800</td>
<td>Wash/screen</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

Rising energy costs will encourage installation of units for short and longer-term storage of solar heat, winter cold energy (for summer air conditioning), off peak power and many
similar measures to conserve energy and or reduce costs. Heat capacitors have an important role to play in the storage of heat (and cold) energy for space heating. The high thermal density of slag, the uniformity and high air permeability and biological inertness suggest a potentially important role for granulated slag in filling compact thermal capacitors.

Hydroponic techniques permit rapid growth of quality market garden produce in urban areas where arable land is in short supply. Granulated slag provides a dense, stable and sterile rooting medium, a uniformly permeable system for transport of a nutrient rich water supply while facilitating easy removal and cleaning of roots. Aquaculture and mariculture (GSA) are rapidly developing technologies for food production. The natural sites suited for such production are limited while there is a desire for improved disease control and hence stock quality and survival rates. [19, 24] These factors are encouraging a search for an economic system in which the aquatic population is isolated from the environment. Granulated slag may have several roles in such a systems including the efficient diffusion of clean oxygenated water into the fish habitat; the filtration and backwashing of effluent solids; and as a rooting medium in a wetland growth and water purification system. The higher capital and energy cost of such a system would have to be offset by lower stock mortality, higher growth rates, premium product quality and waste by-product revenues perhaps including algal fish food production.

The destructive distillation of biomass (carbonization or charring) is receiving fresh attention as a way of producing oil and gas in a renewable way. One difficulty referenced is the formation of tars and coke that tend to build up in the process. Reforming with steam to convert heavy organics to lighter oils and gases requires a catalytic surface in either a packed or fluidized bed. Olivine particles in the 600-1000 micron range have been tested as a catalyst substrate in such systems [5, 26] and appear to have promise in breaking down tar compounds without excessive carbon formation. Copper smelter slag as an end member of the olivine mineral series may be suitable in this application in either a permeable column or a fluid bed operating at high space velocity.

### Copper Smelter Slag Availability

Official global statistics on copper furnace slag production have not been located and may not exist. Figures for copper production, both current (2004) and cumulative production since 1900, are available (ICSG, USGS). The gross copper production figures need to be reduced to account for scrap recycling and hydrometallurgical (leach electrowin) production to provide an estimate of smelter copper production from concentrate.

<table>
<thead>
<tr>
<th>Material</th>
<th>% wt</th>
<th>% Cu</th>
<th>% Fe</th>
<th>% S</th>
<th>% SiO₂</th>
<th>Units Cu</th>
<th>Units Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate + Flux</td>
<td>100</td>
<td>27.5</td>
<td>24.8</td>
<td>26.1</td>
<td>15.8</td>
<td>27.5</td>
<td>24.8</td>
</tr>
<tr>
<td>Furnace Matte</td>
<td>45</td>
<td>60.0</td>
<td>15.0</td>
<td>23</td>
<td>1.0</td>
<td>27.0</td>
<td>6.8</td>
</tr>
<tr>
<td>Furnace Slag</td>
<td>45</td>
<td>1.2</td>
<td>40.0</td>
<td>0.8</td>
<td>33.0</td>
<td>0.5</td>
<td>18.0</td>
</tr>
</tbody>
</table>

The smelter slag production can be estimated by using a copper to slag production ratio (Table 7).
Table 7 indicates $45/27.5 = 1.636$ tonnes of furnace slag produced per tonne copper in smelter concentrate. Additionally based on the iron content of furnace matte an additional $1.636 \times 6.8/18.0 = 0.618$ tonnes converter slag would be produced at 40% iron content. Applying these ratios to the copper production figures given in Table 4 gives the slag production estimates shown in Table 7. A refinement is to divide the slag tonnage estimate between furnace and converter slag.

<table>
<thead>
<tr>
<th>Copper Slag tonnes Factor</th>
<th>2004</th>
<th>Total 1900-2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>1.636</td>
<td>19,000,000</td>
</tr>
<tr>
<td>Converter</td>
<td>0.618</td>
<td>7,100,000</td>
</tr>
<tr>
<td>Combined</td>
<td>2.254</td>
<td>26,100,000</td>
</tr>
</tbody>
</table>

Table 8 recognizes the trend to separate cleaning of converter slag by a variety of means including thermal reduction or grind-flotation rather than reverting the molten slag to the smelting furnace bath. Some converter operations (Mitsubishi process) produce a calcium ferrite in the converter rather than a fayalitic slag. Most converting is still undertaken on a batch basis and therefore the slag tends to be more variable in composition and higher in copper content. Converter slag is not the first choice as a source of fayalitic material.

**Carbon Credits**

Carbon credits are being promoted as one way to encourage improvement in the efficiency of energy use and thereby reduce carbon dioxide emissions to atmosphere. If smelter slag is converted from a waste to a valuable product then a portion of the smelter input energy can be credited to the slag and the imputed energy content of the copper product is proportionately reduced. Additionally if the slag product is used to improve the efficiency of energy use in some application then a further credit would seem to be appropriate. Such credits may arise from providing an alternative material e.g. displacing cement; conserving resources e.g. heat or water; or raising productivity e.g. farm or aquaculture efficiency.

**Exploring Opportunities**

The merit of challenging the global technical, scientific and entrepreneurial community to identify potential beneficial uses for smelter slag with the offer a prize for suggestions that lead to commercial success in establishing substantial new markets should be considered as one way forward. This would build on an approach pioneered by Barrick Inc. in connection with the Valadero silver bearing deposit and might be structured in a similar way.

**SUMMARY**

Granulated smelter slag has a unique combination of properties that suggest it may find valuable markets in a number of emerging industries including those linked to energy, food production and water conservation and water purification. Fayalite is a rare mineral in nature and once profitable and environmentally acceptable uses for copper smelter slag are established, a floor price may be established by the cost of synthesis from raw materials in a stand-alone plant. The likelihood of the smelting industry qualifying directly for a carbon credit appears remote even though is generates heat from a non-carbon fuel
source (iron sulphide). However the industry could benefit indirectly from innovation incentives leading to new energy, food and water conservation technologies that will provide prime markets for granulated smelter slag. The identification and development of these opportunities require encouragement of the technical-scientific-entrepreneurial community to focus on slag properties and uses. The owners of the slag, the smelting industry, are in the best position to encourage this interest perhaps through an open competition.

CONCLUSIONS

Global energy, food and water challenges are encouraging the development and rapid growth of new industries. Some of these new industries may provide large opportunities for profitable slag sales. Realizing these opportunities requires that the properties of slag be documented and circulated to create an awareness in the scientific/entrepreneurial community of this resource and the interest of smelting industry establishing profitable and environmentally acceptable markets. The organization of a web based challenge with an appropriate reward for productive proposals is an initial approach deserving consideration by the industry. The possibility that slag sales could also provide industry with a basis for tangible or implicit carbon credit provides an additional incentive for slag marketing.

REFERENCES


