# Further processing and granulation of slags with entrained metal and high metal compound content, with specific reference to present manganese slag dumps as well as additions due to daily production

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**Abstract** – Water granulation of certain slags with high metal entrainment has customarily not been practised, not only due to the belief that such processes are too dangerous and unproven in the pyrometallurgical industry, but also that it might not be economically viable or environmentally acceptable.

General slag granulation, on the other hand, is extensively applied, although in some cases crudely, with disastrous effects, as a result of not recognising the high heat capacities prevalent in slags. Thus, purpose-designed granulation and solidification processes are discussed, taking into account specific applications and the individual signatures of alloys and slags, emphasising that no slag, matte, or alloy responds in similar fashion to a granulation practice.

This paper addresses three issues, namely:

- Water-granulation of BOF steel slag, without processing it to render it environmentally safe, physically and chemically acceptable for use by the construction industry, and the process economical
- Processing air-cooled BOF steel slag to change its physical and chemical properties to be acceptable for various uses and extracting metallic and bound iron
- Processing air-cooled or molten manganese slag to lower its manganese content to a level that is acceptable from an environmental and health point of view, and extracting FeMn-alloy of acceptable composition.

The latter process culminated in a patented process to extract FeMn from air-cooled and molten manganese slag, and, at the same time, produce a hydraulic (cementitious) slag, thus transforming a possible hazardous by-product into virtually 100% saleable products.

### INTRODUCTION

Modern conservation principles frown upon the dumping of liquid slag on dumps, due to the many undesirables contained in slags that can leach into the ground water. The only time that this will be allowed is if a properly designed slag dump is constructed of which the capital and running costs are way in excess of those of a slag granulation plant.

Processing of such slag-dumps is very labour intensive and costly, where crushing and screening plants are utilised to reduce the slag-dumps by either recycling or jigging to remove alloys, or to convert it into a backfill material or aggregates for other applications.

Granted, slow cooling of slag renders it fit for removal of included alloys while sudden quenching in the water granulation process traps the included alloy in the granule so that only milling of the slag can liberate such alloy. However, these processes do not result in the recovery of metals present in the slag as oxides or silicates; for example, the total Fe content of BOF slag can be 31.3% Fe<sub>2</sub>O<sub>3</sub> while the metallic Fe content is only 2.3%.

Should slags be dumped with no re-use, such an operation often requires a bigger capital investment than a granulation plant. A properly designed substratum is required for such a slag dump for many ferro-alloy slags, to prevent leaching of unwanted chemicals into the subsoil. Haul roads with extremely shallow slopes must be built to accommodate slag carriers. Slag carriers have to be acquired, maintained, and eventually be replaced, whereas water granulation requires only a de-watering system and normal trucks or conveyors to remove the product.

It therefore makes sense to ensure that a properly designed water granulation system is installed from the outset, to prevent costly downtime, production interruption, and therefore income losses that could cripple a smelter operation.

The latest processes supersede this inefficient method by using slag-cleaning furnaces to ensure that alloys are removed via a pyrometallurgical process for high-value alloy slag. This separates and melts the alloy, and produces a clean slag, eliminating the crushing, screening, and milling requirement. The objectives of the investigation were amongst others to:

- (i) Find a use for air-cooled Mn-slag dumps in a quantity that would eliminate continued increase in dumped material due to fresh arisings; and
- (ii) Reduce its hazardous rating before being utilised by the building and construction industry;

in accordance with the integrated Waste Management plan, as outlined in the National Waste Management Strategy (1999) and the White Paper on Integrated Pollution and Waste Management (2000).

In order to achieve this economically, the process would have to be able to:

- a) recover FeMn alloy of the desired composition from the (Ca,Mn)SiO<sub>4</sub> in re-melted Mn slag;
- b) water granulate the slag so that it can be used in its unmilled or milled form, respectively as sand for concrete products or as a

supplementary major constituent of common Portland cement, and as a cement extender in concrete.

Where circumstances require the slag to be dumped and air cooled, provision is made for the storage of the product in a surfaced bunded area to be crushed as aggregate for concrete and roads.

#### CONVENTIONAL WATER GRANULATION DEVELOPED FOR EACH SPECIFIC APPLICATION BASED ON IMPROVED TECHNOLOGIES, MODELLING AND APPLICATION

Before any granulator design can be attempted, the metallurgical composition of the specific alloy or slag must be analysed with respect to its enthalpies in a molten, sub-molten, and frozen state. Elemental analyses of the alloy or slag are not sufficient for final design parameters, as the impact of all species on the granulation process must be assessed.

The likelihood of SREs, (Sudden Release of Energy) must be understood and appreciated, as such a SRE can have devastating effects in a poorly designed granulation plant.

This phenomenon refers to a sudden explosion-like expansion that can sometimes occur spontaneously between hot molten metal and water. It is a well-known problem in poorly designed granulation processes. The mechanism of this process is described as follows; a pocket of water gets surrounded by hot metal, and the water rapidly increases in temperature until it becomes superheated, and suddenly converts to superheated steam that expands rapidly.

One might postulate that the resultant rapid gaseous expansion may be exacerbated if the atoms of hydrogen and oxygen within a water molecule become so highly energised that the divalent bonds between the covalently bonded hydrogen molecule and the oxygen atom break momentarily, liberating hydrogen and oxygen. Both of these elements are gases at ambient temperature and as such expand rapidly at the elevated temperature liberating the energy and immediately begin to cool. This event takes place in a highly oxidising environment and the hydrogen and oxygen recombine and give rise to significant volume changes within an extremely short time frame, in the order of 0.1 milliseconds. The volume changes associated with these mechanisms then propagate as a pressure front at very high velocities. This pressure front may then initiate further such interactions at neighbouring metal-water interfaces, so propagating the volume change. It is believed that no significant chemical alteration takes place and it is thus classified as a physical phenomenon, not a chemical explosion.

# Basic water jet configuration

The possibility of steam generation at a point of contact must be assessed, as a decision must be made whether this alloy or slag can be granulated successfully

with higher-temperature water, or if lower-temperature water must be used to prevent hydrogen formation and steam entrapment that can cause SREs.

Once these design parameters have been established, the best method of granulation can be selected, based on the initial calculation and predicted behaviour of solidus temperature and viscosity of the alloy or slag in question. Under no circumstances should it be assumed that one slag or alloy will react the same as another.

Generically, water granulation involves breaking up a stream of molten metal or slag by means of a water jet.

The molten metal/slag is poured into a hot runner conveying it to drop vertically down into a horizontal stream of water, which breaks the molten metal/slag flow on contact into small particles.

Quenching of the molten metal/slag particles is achieved in different ways, depending on the configuration of the stream of water and whether the stream is projected into an immediate granulation tank or carries the particles down a launder to a tank.

The point of contact between the liquid metal/slag and the water stream is of major importance, as excessive penetration of the liquid metal/slag into the water stream could lead to the melt stream not being adequately fragmented, resulting in the molten stream 'punching' through the water jets. In the case of tank granulation, the melt will enter the water bath as a large mass if it has punched through the water jet, and the melt will then partly break up from thermal shock, resulting in sizeable molten pieces forming a frozen shell with the nucleus remaining molten while it falls to the bottom of the granulation tank. Impact could then fracture the shell, resulting in the quenching of the molten metal/slag while trapped under water, where the resultant trapped super-heated steam can be the cause of a SRE.

To mitigate this risk, one could granulate down a launder with no water bath at the point of granulation but the melt penetrating through the water jets can build up in the bottom of the launder where its surface will solidify but it will remain molten inside posing a risk where trapped super-heated steam will develop, resulting in a massive SRE.

If the water stream were still intact at the time that the melt stream intersected the water stream, the break-up would occur from the high speed of the water tearing the melt stream apart. According to the Weber criterion, the average diameter of melt droplets that would then be formed would be about  $10 \,\mu\text{m}$ . However, we know in practice this is not the case, hence we must assume that the water stream breaks up into droplets before interacting with the melt and the resulting coarse spray causes the melt stream to break up into droplets/particles. The Weber number determines the size of the water droplets, given that the motion of the water stream through the (relatively)

stationary air causes the break-up. It can therefore be shown that the water droplets formed will be typically about 2 to 5 mm in diameter. A fair assumption would be that the size of the particles formed in the melt stream by these water droplets would have a similar mass to the water droplets.

It is believed that the size of the water droplet could become an issue if they are very large compared to the thickness of the water jet. If the water droplets become relatively large in this way, they are then likely to be spaced out with significant gaps between them, which may lead to gaps in the water stream through which sizeable volumes of the melt stream may fall.

# Particle quenching

During the quenching process, the slag or alloy transforms through all the phases which it went through during the smelting process, but in this case just in a reverse mode, hence it follows that certain elements in the molten slag or alloy which have a much higher solidus than others would require bigger volumes of quenching agent at that moment. Once in a total liquid mass, the elements and species are all mixed together, but as this slag or alloy mass is suddenly quenched, different species are liberated in milliseconds and can act quite differently, depending on the quenching method employed.

# **GRANULATION OF SLAGS WITH HIGH METAL ENTRAINMENT**

Granulation of blast-furnace slag to increase the cementitious values to be used as a cement extender is successfully practised widely in the world. However, this commodity has become scarce and some countries have resorted to importing granulated blast-furnace slag to meet their needs.

Steel smelters that produce steel via the BOF route have to date found no specific reason to granulate the BOF slag except for utilising the granulated slag for a fertiliser which as far as could be determined, only one smelter in Europe installed such a plant which has long since been shut down. In the past, it has also been used for road construction, though this use is declining because of problems created by the slag's unsoundness. Other uses include general construction and landfill applications.

A major reason for not water granulating BOF slag was that the Fe will be trapped in the matrix whereas, with air-cooling, the Fe can be removed via magnetic separation. A further reason was that the high Fe inclusion made for high risks of explosions when the BOF slag is water granulated.

Today, massive slag dumps are creating an environmental problem, and daily production just adds to the dilemma. By re-smelting the existing BOF and arc furnace slag dumps, the entrained metals can be recovered, and the slag can be granulated to yield a cementitious slag similar to blast-furnace slag.

Due to the relatively low monetary value of the recovered iron units, the submerged arc furnace route is not economically viable; therefore it is possible

that ailing SRT (Smelting Reduction Technology) processes can be exploited for this purpose.

## Granulation of untreated Basic Oxygen Furnace slag

Granulation of BOF slag for use as a cement extender is rare, because its chemical composition is not amenable to quenching it as glass, and also because free CaO and MgO tend to be present, which causes it to be unsound, that is, it expands when it comes into contact with water. In addition, the hydraulic (cementitious) reactivity is not as good as that of granulated blast-furnace slag. Furthermore, the chances of reducing the iron oxide and free Fe of the untreated slag significantly are doubtful. However, since the granulation by water of aircooled BOF steel slag had received serious attention during the past decade or more because of pressure from environmentalists on industries to utilise industrial by-products, it was decided to conduct tests in a launder granulation pilot plant with an over-under water jet configuration, where the upper jet will break the melt into sufficiently small particles which will then migrate to the lower jet as the main quenching volume. This is the most efficient and effective method of granulation whereby the quenching water temperature can be accurately controlled to promote virtually instantaneous quenching.

To be able to have a reference point, air-cooled BOF slag was smelted in a submerged arc furnace and the slag granulated in a launder granulation pilot plant, as described above, where after the reclaimed Fe was tapped separately.

The chemical and mineralogical composition of the BOF slag before and after water-granulation is shown in Tables I and II respectively.

Analyte		Air-cooled	Granulated
		BOF slag	BOF slag
SiO <sub>2</sub>	%	13.1	12.4
TiO <sub>2</sub>	%	0.49	0.45
K <sub>2</sub> O	%	< 0.1	0.01
MgO	%	8.65	8.30
Al <sub>2</sub> O <sub>3</sub>	%	4.62	5.53
Fe <sub>2</sub> O <sub>3</sub>	%	31.3	27.7
CaO	%	36.7	35.9
MnO	%	5.44	6.94
P <sub>2</sub> O <sub>5</sub>	%	1.09	1.02
Na <sub>2</sub> O	%	< 0.05	< 0.05
Cr <sub>2</sub> O <sub>3</sub>	%	0.17	0.16
$V_2O_5$	%	0.08	0.09
LOI	%	-2.91	-0.61
Total	%	98.7	97.9
Total S	%	0.08	< 0.01

**Table I:** Comparative chemical analysis of untreated aircooled and water-granulated BOF slag

Sulfide S	%	0.02	< 0.01
SO <sub>4</sub>	%	< 0.4	NA
Total C	%	0.20	0.04
CO <sub>3</sub>	%	0.55	NA
Total Organic C	%	0.11	NA
Metallic Fe	%	2.32	0.28
CaO/SiO <sub>2</sub>	-	2.80	2.90
$(CaO + MgO + Al_2O_3)/SiO_2$	-	3.82	4.01
$(CaO + 1.4MgO + 0.65Al_2O_3)/SiO_2$	-	3.93	4.08

NA = Not analysed for this constituent

Table II:	Comparative mineral composition of untreated air cooled and
	water-granulated BOF slag

Mineral phase	Approximate chemical formula	Air-cooled BOF slag	Granulated BOF slag
Akermanite- gehlenite	Ca2(Mg,Al)(Si,Al)2O7	-	-
Hedenbergite	CaFe(Si <sub>2</sub> O <sub>6</sub> )	-	3% to 10%
Fayalite	FeMgSiO <sub>4</sub>	3% to 10%	-
Grossularite	$Ca_3Al_2Si_3O_{12}$	<3%	-
Wuestite	FeO	>50%	10% to 20%
Larnite	Ca <sub>2</sub> SiO <sub>2</sub>	20% to 50%	20% to 50%
Merwinite	Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>	3% to 10%	-
Mayenite	$(CaO)_{12}(Al_2O_3)_7$	3% to 10%	10% to 20%
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	-	-
Mn-magnetite	(Fe,Mn)O.Fe <sub>2</sub> O <sub>3</sub>	-	20% to 50%
Ca-Mg-ferrite	(Ca,MgO).Fe <sub>2</sub> O <sub>3</sub>	-	10% to 20%
Spinel	MgOFe <sub>2</sub> O <sub>3</sub>	3% to 10%	-
Periclase	MgO	<3%	-
Hematite	Fe <sub>2</sub> O <sub>3</sub>	<3%	-
Fe Metal	Fe	3% to 10%	<3%
Graphite	С	<3%	-
Glass	??	<3%	3% to 10%

- : Means not detected

The main observations from the chemical and mineralogical analyses were the following.

- (i) The free Fe content of the granulated slag was 0.82% compared with 2.32% of the air-cooled slag.
- (ii) The Fe<sub>2</sub>O<sub>3</sub> content of the granulated slag was only 3.6 percentage points less than that of the air-cooled slag, namely 27.7% compared to 31.3%.
- (iii) A major proportion of the wuestite and all of the fayalite of the aircooled slag was converted to hedenbergite, Mn-magnetite and Ca-Mgferrite in the granulated slag.

(iv) The estimated glass content of 3 to 10% of the granulated slag, compared with < 3% in the air-cooled slag, proved that the chemical composition of the BOF slag did not lend itself to high glass content even if it is granulated under ideal conditions.

Property		Granulated BOF			
				CEM I	
		SSA 4 040 cm <sup>2</sup> /g			42.5
		20%	35%	50%	
Compressive	2 days	10.5	0.8	0.9	24.7
strength, MPa, at	7 days	26.4	14.3	1.2	39.4
	14 days	34.6	24.5	11.7	42.0**
	28 days	43.2	29.0	23.2	50.4
% of CEM I strength at 28 days		85.5	57.4	45.9	100.0
Initial setting time, minutes		165	164	47	NA
Soundness, mm		0.0	0.5	1.0	NA

**Table III:** Compressive strength, initial setting time and Le Chatelier soundness of CEM I and CEM I/granulated slag blends

\*\*: Interpolated value

SSA = Blaine specific surface area

NA = not available

The following were concluded from the results in Table III.

- (i) The 20% and 35% blends complied with the EN 197 requirements for setting time, but not the 50% blend.
- (ii) Although the le Chatelier soundness of all the blends complied with the maximum limit, the autoclave test proved that the granulated slag was unsound and therefore unsuitable for use as cement replacement material or as aggregate.
- (iii) The 20% blend complied with the requirements for CEM II A-S 32.5R as well as with the ASTM activity index of 75% at 28 days. The 35% and 50% blends did not meet the strength requirement of the lowest EN strength class.
- (iv) The hydraulic (cementitious) properties of the slag were probably due to the presence of larnite (Ca<sub>2</sub>SiO<sub>4</sub>).

The results proved, as was suspected, that the chemical composition of the slag will have to be modified to be closer to that of blast-furnace slag, and coal will have to be added to reduce ferrous and ferric iron to metallic iron.

This process will be possible in any of the SRT furnaces available; however, the economics will have to be assessed to find the optimal economical SRT furnace process.

# Granulation of processed Basic Oxygen Furnace slag

BOF slag, which was blended with 22% silica sand to reduce the CaO/SiO<sub>2</sub>, and 11% coal added for reduction, was smelted in a submerged arc furnace and granulated in the same configured granulation pilot plant as above.

110 kg metal was recovered. A secondary electron image of the granulated modified slag is shown in Figure 1. The results that were obtained are presented in Tables IV, V, and VI.

The following were concluded from the results.

- (i) The addition of silica resulted in a reduction of the CaO/SiO<sub>2</sub> from 2.77 in air-cooled BOF slag, to 0.90 in the granulated modified slag and of the (CaO + MgO)/SiO<sub>2</sub> from 3.39 to 1.30, thus making the melt amenable to granulation and the formation of glass and a product that was sound, in other words without free lime or periclase (free MgO). The composition of the modified slag fell within the field of blast-furnace slag in terms of the ternary plot of CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>.
- (ii) The use of coal as a reducing agent resulted in the reduction of iron oxides in and the recovery of iron metal from the minerals wuestite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), brownmillerite, (Ca<sub>4</sub>Al<sub>2</sub>Fe<sub>2</sub>O<sub>10</sub>), and fayalite ((Fe,Mg)<sub>2</sub>SiO<sub>4</sub>).
- (iii) The granulated slag complied with all the requirements of SANS EN 50197-1:2005 and SANS 1491-1989, Part I for granulated blast-furnace slag.

Analyte		Air-cooled BOF slag <sup>1</sup>	Granulated BOF slag + SiO <sub>2</sub> + coal <sup>2</sup>
SiO <sub>2</sub>	%	13.3	36.3
Al <sub>2</sub> O <sub>3</sub>	%	5.24	6.36
Fe <sub>2</sub> O <sub>3</sub>	%	33.00	1.85
MnO	%	3.61	7.41
TiO <sub>2</sub>	%	0.51	0.36
CaO	%	36.8	32.8
MgO	%	8.33	14.3
$P_2O_5$	%	0.87	0.05
Total S	%	0.14	0.29
$Cr_2O_3$	%	0.38	0.06
V <sub>2</sub> O <sub>5</sub>	%	0.1	0.01
K <sub>2</sub> O	%	< 0.01	< 0.01
Na <sub>2</sub> O	%	< 0.05	< 0.05
LOI	%	-2.71	-0.95
Total	%	99.4	98.5

**Table IV:** Comparative chemical composition of aircooled and granulated modified BOF slag

SO <sub>4</sub>	%	< 0.4	NA
Total C	%	0.17	0.02
CO <sub>3</sub>	%	0.48	< 0.01
Total organic C	%	0.08	< 0.05
Metallic Fe	%	2.1	1.05
CaO/SiO <sub>2</sub>	-	2.77	0.90
(CaO+MgO)/SiO <sub>2</sub>	-	3.39	1.30

<sup>1</sup>: SGS Mineralogical Report: No. MIN 0805/61 30/09/2005

<sup>2</sup>: SGS Mineralogical Report: No. MIN 0805/76 30/09/2005

NA = Not analysed for this constituent

Silica sand: >99% SiO<sub>2</sub>



Figure 1: Secondary electron image of granulated modified (BOF + SiO<sub>2</sub>) slag

Mineral phase	Approx. chemical formula	Air-cooled BOF slag <sup>1</sup>	Granulated (BOF + SiO <sub>2</sub> + coal) slag <sup>2</sup>
Fayalite	(Fe,Mg) <sub>2</sub> SiO <sub>4</sub>	<3%	ND
Grossularite	Ca <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	<3%	ND
Larnite	Ca <sub>2</sub> SiO <sub>4</sub>	20 - 50%	ND
Merwinite	$Ca_3Mg(SiO_4)_2$	<3%?	ND
Mayenite	$(CaO)_{12}(Al_2O_3)_7$	3 - 10%	ND
Brownmillerite	Ca <sub>4</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>10</sub>	3 - 10%	ND
Wuestite	FeO	20 - 50%	ND
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	20 - 50%	ND
Hematite	Fe <sub>2</sub> O <sub>3</sub>	20 - 50%	ND
Fe metal	Fe	3 - 10%	<3
Glass	??	3 - 10%	98%

**Table V:** Comparative mineralogical composition of air-cooled and granulated modified BOF slag

<sup>1</sup> (SGS Mineralogical Report: No. MIN 0805/61 30/09/2005)

<sup>2</sup> XRD Analytical and Consulting

ND = Not detected

**Table VI:** Physical properties of the milled granulated modified BOF slag compared to the requirements of SANS 501491-1: 2005 for ground granulated blast-furnace slag

Property		Requirement	Granulated modified BOF slag
Specific surface, $cm^2/g$		3 500	4 000
Reactivity, compressive	7 days	12	24
	28	32.5	45.4
strength, wir a, min. at	days		
Reactivity with lime hydrate,	Б	11	
compressive strength, MPa, min.ª		5	14
Glass content, % (by mass), min.		95 <sup>b</sup>	98c
Soundness, expansion, mm, max		10	1

a The methods described in point 6 of BS 6699:1992 and SANS 50196 were used to determine the compressive strength and interpret the result.

b SABS 1491: Part I-1989

c The requirement of EN 197-1 is 67%

#### Granulation of processed ferromanganese slag

The main component of air-cooled ferro-manganese slag is glaucochroite,  $(Ca,Mn)_2SiO_4$ , which has the same structure as the cement mineral, belite,  $Ca_2SiO_4$ . Glaucochroite has hydraulic properties but, because of its high Mncontent, it is classified as hazardous waste. In addition, the rate of strength development of the milled air-cooled slag is slow. Smelting the air-cooled slag and treating it with a view to recover FeMn alloy and granulating the slag is economically a viable proposition, because of the suitability of the granulated slag for use at as a cement extender and value of the recovered alloy.

To establish the feasibility of such a process, a mixture of FeMn slag, BOF slag, and coal was smelted in a submerged-arc furnace and granulated in the same configured granulation pilot plant as previously mentioned. The chemical analyses of the feed materials and the processed FeMn slags are presented in Table VII. The mineralogical properties are shown in Table VIII, and some of the cementitious properties are summarised in Table IX. Figure 2 is a back-scattered electron image of the granulated slag.

The results showed the following.

- (i) The MnO content of the granulated processed FeMn slag was 6.1%, compared with 21.8% of the air-cooled slag.
- (ii) The Mn in the CaMn-silicate was recovered as FeMn alloy.
- (iii) The granulated slag was composed practically of glass only, and complied with all the requirements of SANS EN 50197-1:2005 and SANS 1491-1989, Part I for granulated blast-furnace slag.

	Fee	Feed materials				
Analyte		Air-cooled Air-cooled		Casl	processed	
		FeMn slag <sup>1</sup>	BOF slag <sup>2</sup>	Coal	<b>FeMn slag</b>	
SiO <sub>2</sub>	%	31.5	7.56	7.56	31.8	
Al <sub>2</sub> O <sub>3</sub>	%	4.18	4.46	4.46	6.59	
Fe <sub>2</sub> O <sub>3</sub>	%	2.58	0.58	0.58	0.71	
MnO	%	21.80	ND	ND	6.11	
TiO <sub>2</sub>	%	0.15	0.30	0.30	0.18	
CaO	%	32.0	1.68	1.68	37.2	
MgO	%	7.3	0.35	0.35	14.4	
$P_2O_5$	%	< 0.01	0.42	0.42	< 0.01	
Total S	%	0.86	0.80	0.80	0.76	
Cr <sub>2</sub> O <sub>3</sub>	%	0.01	ND	ND	0.02	
V <sub>2</sub> O <sub>5</sub>	%	< 0.01	ND	ND	< 0.01	
K <sub>2</sub> O	%	0.14	0.12	0.12	< 0.01	
Na <sub>2</sub> O	%	0.24	0.03	0.03	< 0.05	
LOI	%	-2.63	79.18	79.18	-1.22	
Total	%	97.3	96.15	96.15	95.8	
SO <sub>4</sub>	%	< 0.4	-	-	ND	
Total C	%	0.16	-	-	0.29	
CO <sub>3</sub>	%	0.17	-	-	0.11	
Total organic C	%	0.13	-	-	0.27	
Metallic Fe	%	0.44	-	-	0.82	
CaO/SiO <sub>2</sub>	-	1.02	0.22	0.22	1.17	
(CaO+MgO)/SiO <sub>2</sub>	-	1.25	0.27	0.27	1.62	

**Table VII:** Chemical analysis of feed materials and granulated processed FeMn slags

<sup>1</sup>: SGS Mineralogical Report: No. MIN 0805/61 30/09/2005

<sup>2</sup>: SGS Mineralogical Report: No. MIN 0805/76 30/09/2005

ND = Not determined

21% FeMn alloy was recovered from the total FeMn and BOF slag charge. The chemical composition was: 71.8 % Mn, 18.5% Fe, 2.35% Si, and 56.2% C. A mass balance of the slag and metal was not done.

Mineral Phase	Approx Chemical Formula	Air-cooled FeMn slag <sup>2</sup>	Granulated processed
		0	FeMn slag
Glaucochroite	(Ca,Mn) <sub>2</sub> SiO <sub>4</sub>	<50%	ND
Akermanite-	$C_{22}(M_{C},\Lambda^{1})/(S;\Lambda^{1})_{2}O_{2}$	10 20%	ND
gehlenite	Ca2(1v1g,A1)(51,A1)207	10 - 20 %	
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	<3%	ND
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	3 - 10%	ND
Fe metal	Fe	<3%	ND
FeMn metal	FeMn	<3%	ND
Glass	??	<3%	<b>99.2</b> % <sup>3</sup>

Table VIII: Mineralogical composition of air-cooled and granulated processed FeMn slag<sup>1</sup>

<sup>1</sup> (SGS Mineralogical Report: No. MIN 0805/61 30/09/2005)

<sup>2</sup> Semi-quantitative XRDA

<sup>3</sup> Microscopy

Table IX: Physical properties of milled modified granulated FeMn slag compared to the	9
requirements of SANS 501491-1: 2005 for ground granulated blast-furnace slag	

			Modified
Property		Requirement	granulated
			FeMn slag
Specific surface, cm <sup>2</sup> /g		3 500	4 000
Reactivity, compressive	7 days	12	27
strength, MPa, min. at	28 days	32.5	49.2
Reactivity with lime hydrate, compressive		5	24
strength, MPa, min.ª			
Glass content, % (by mass), min.		95 b	96 <sup>c</sup>
Soundness, expansion, mm, max		10	1

<sup>a</sup> The methods described in point 6 of BS 6699:1992 and SANS 501976 are used to determine the compressive strength and interpret the result.

<sup>b</sup> SABS 1491: Part I-1989

<sup>c</sup> The requirement of EN 197-1 is 67%



Figure 2: Secondary electron image of granulated modified FeMn slag

# ANGEL'S HAIR FORMATION IN HIGH-SILICA SLAGS

Angel's hair, also known as slag wool, is the general term for fibrous tails formed behind particles during their flight in the granulation water jets. These tails break off and attach themselves to crevices and protrusions in the system. Being light, they are also present in the steam generated by the granulation process and are then airborne and drift down onto the plant where they get lodged onto ledges and horizontal surfaces.

Slags with a high SiO<sub>2</sub> content are normally prone to forming angel's hair.

The presence of excessive angel's hair is normally a sign that granulation water pressures are not correct, water temperature is too high, and particles are quenched too slowly – brought about by the nozzle and bath configuration.

Formation of angel's hair cannot be totally eliminated. However, proper granulation practices and technologies, dependent on the type of slag and the  $SiO_2$  content, can reduce the formation. It is, however, prudent to provide a cooling system that can cope with angel's hair, as all the ideal parameters cannot always be kept to optimal requirements, and angel's hair will form with the slightest of deviations.

Specially designed cooling towers are being used all over Europe, especially in the blast-furnace slag granulation field where angel's hairs are very prominent. These open spray-cooling towers are normally of concrete construction, due to the massive water flows required for blast-furnace slag granulation where slag flows are 5 to 10 tons/minute.

Where smaller slag flows are evident, such as in the non-ferrous industries, specially designed open-spray modular cooling towers can be used successfully, being more economical than concrete structures.

Cooling towers with a fill material will be affected whereby angel's hair would block the passage of water, resulting in fines in the water accumulating on this blockage. This, in turn, reduces the capacity of the cooling tower, reducing the effectiveness, which results in increased temperatures that are one of the factors for the promotion of angel's hair formation.

Steam generation at the point of granulation must be avoided, as the rising hot air and vapour will promote the angel's hair to an airborne state, thus spreading the fibrous tails over a wide area where they can block any water system and become a major hazard.

# CONCLUSIONS

Each metal or slag has its own chemical and, therefore, thermal characteristics.

In so far as smelting and melting techniques and methods differ from alloy to alloy, so too do the solidification processes differ between alloys and their associated slags. Why is it then so often believed, or assumed, that the solidification characteristics will be similar in divergent alloys?

Solidification can be termed as the attempt at controlled transfer of energy under potentially explosive conditions, and the process must therefore be treated as such during the process design stage.

Metal and slag solidification, be it in lump form or atomisation, is an extremely elegant process to reduce process steps where costly high-maintenance, mechanical equipment is required, and should therefore be exploited to its fullest, utilising the fit-for-purpose process for each required application. Granted, molten metal and slag and water are not the most desirable compounds to be brought together, but water still remains the best quenching medium, despite a multitude of alternative processes developed to substitute water with air, moist air, spinning cups with fluidized beds and the like.

If it is well designed, a water granulation plant is far safer than any other granulation process.



## David Norval

1978: Joined Bateman as a Civil Engineer

1981–1987: Construction Manager and later Project Manager mainly on Iron and Steel and Petrochemical related projects

1987–1992: Project Manager and Deputy Construction Manager, Mossgas onland project

1993-: Operations Manager for Bateman Iron & Steel Technology (Pty) Ltd with main activities in blast furnace feeding systems and blast-furnace slag granulation and de-watering systems

1994–: Operations Director, Iron & Steel Technology (Pty) Ltd with main focus on slag and matte granulation, metal atomisation, and de-watering processes

General Manager, Post Tap-hole Services, a joint venture between Mintek and Bateman for solidification processes, tapping equipment, and ladle metallurgy and handling

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2003–: Manager Post Tap-hole Services, Pyrometallurgical Technologies, a process division within Bateman Engineering Projects

2006- Senior Project Manager, Bateman Engineering Projects, various major projects

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