

Hot metal desulphurisation

As the demand of ever lower steel sulphur levels continues, the use of hot metal desulphurisation remains the most cost effective way of removing sulphur in the BOS process. Today lime, calcium carbide and magnesium are the main reagents used via injection into transfer ladles. Optimum performance is achieved with mixtures of these materials rather than individual injection.

AUTHOR: Wolfgang Gitterle
Almamet

With the exception of machining steels, sulphur is undesirable in steel because of embrittlement during manufacture and use. As the demand for ever lower steel sulphur levels increases so the need for lower hot metal sulphur levels has increased, this being the most cost effective desulphurisation method currently available. Today hot metal is regularly desulphurised to below 100ppm, and in some steel plants, to 10ppm. As well as the increased requirements of steel quality, reduced scrap quality and increasing cost of high quality iron ores are reasons which necessitate desulphurisation of hot metal.

Over time many desulphurisation agents have been developed to provide hot metal desulphurisation in a cost efficient way. The main reagents will now be described, together with their advantages and disadvantages.

SODA

During the 1960s, soda (sodium carbonate, Na_2CO_3) was a popular desulphurisation agent. Due to the easy application method - the soda was delivered in paper sacks and, according to requirements, placed in the empty ladle before pouring the hot metal - this desulphurisation method could easily be used in every plant. However, considerable problems arose due to the decomposition of the carbonate in contact with the liquid iron, producing acrid sodium oxide fumes. These are harmful to health and fume extraction systems were generally inadequate. A further environmental disadvantage resulted from the arising soda slags which were water soluble, leading to leaching and ground contamination.

Today, soda desulphurisation is practically no longer used apart from occasional use as a fluxing agent to reduce the iron losses when deslagging the treatment ladles. For this purpose soda is either placed in the treatment ladle, added in several desulphurisation mixtures or injected into the hot metal as a third component at the end of a desulphurisation treatment.

Component	Recommended range %
CaO	92 - 98
MgO	0.5 - 2.0
SiO ₂	0.1 - 1.0
S	max. 0.1
CO ₂	max. 2.0
H ₂ O chemically combined	max. 1.5
Ignition loss	max. 2.5

Table 1 Chemical analysis of lime

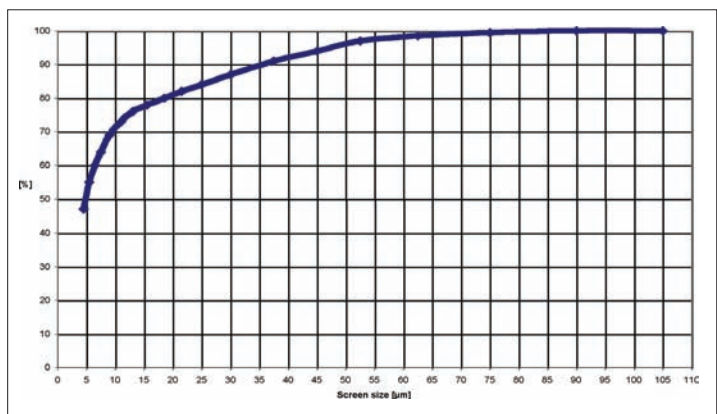


Fig.1 Grain size distribution of lime

LIME

Lime (CaO) is the most important calcium source in steel production and is widely available naturally as limestone, CaCO_3 . Its use in hot metal desulphurisation is in the burnt condition; if unburnt limestone is used, CO_2 is produced following contact with the hot metal and the oxygen activity in the hot metal rises considerably, so reducing the efficiency of the desulphurisation agents.

Lime is made by burning limestone in shaft or rotary kilns, then ground to below 100µm. Very fine grains are unsuitable for injection so alternative uses of this material are via conditioning the lime grains so as to be suitable for injection or using the lime in the sintering plant. Table 1 and figure 1 show a typical analysis and grain size of a lime suitable for hot metal desulphurisation.

Lime has problematic conveying characteristics in the granulation size necessary for hot metal desulphurisation,

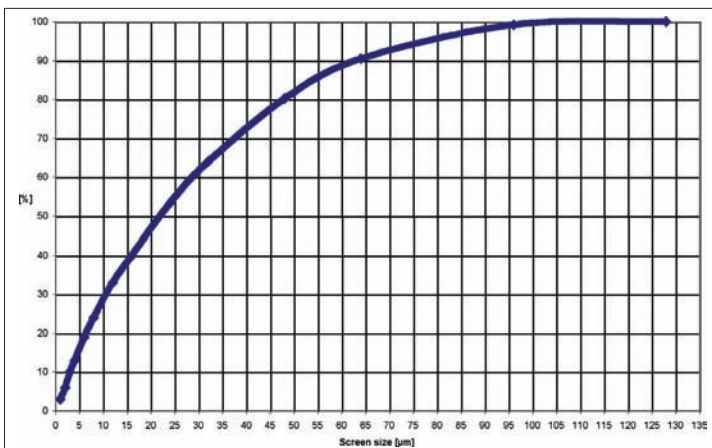


Fig.2 Grain size distribution of a typical calcium carbide mixture

and is also adversely affected by moisture, leading to nozzle blockages and/or irregular flow characteristics. To counteract these tendencies the lime grains are surface treated with special oils.

Lime is the cheapest hot metal desulphurisation agent used today, however, it has a lower effectiveness. It also produces the largest quantity of slag and, as iron losses are proportional to slag weight, this too adversely affects the cost. These slags do have a lower viscosity than those from calcium carbide injection and they decompose more readily, thus they can be more easily treated without having to add fluxing agents. A further advantage is the fact that lime is not subject to dangerous goods regulations and there are no transport and handling problems.

Today lime is primarily used in combination with other agents, principally magnesium.

CALCIUM CARBIDE

In the 1970s, calcium carbide was introduced as a hot metal desulphurisation agent, since when it has become one of the most popular, especially in Europe, where consumption is estimated at approximately 100,000tpa.

Calcium carbide is made from coke and lime in an electric arc furnace. Approximately 950kg of lime and 600kg of coke are necessary to produce one tonne of calcium carbide; with a specific power requirement of about 3200 kWh/t. After the calcium carbide has solidified in chill moulds, it is crushed and classified, with the coarse fractions mainly serving as base material for acetylene generation. The finer material is ground with high volatile coals, other gas separators, lime and fluxing agents, in mills to a granulation below 100µm. The gas separators are used to providing a high dispersion of the desulphuriser in the hot metal.

Initially carbide mixtures with approximately 50% CaC₂ with 10% calcium carbonate as a gas separator (the balance was mainly lime), were used for torpedo desulphurisation. With the introduction of transfer ladle treatment, mixtures with approximately 70% CaC₂ with 5% gas separators and lime as the balance material, are

mainly used as higher gas flow rates can be obtained compared to torpedo injection, and greater CaC₂ efficiency is obtained. As the use of calcium carbonate causes an increase in oxygen activity, high volatile coals have tended to replace limestone as the gas separator material, thus increasing desulphurisation efficiency. Also during the injection into the hot metal, carbon will split off from the CaCO₃ and become bound into the slag. Then when tilting the slag onto the dump, this finely distributed graphite combusts, and excessive smoke arises.

Since desulphurisation is a diffusion-controlled reaction, and related to the reactive surface area available for reaction, the desulphurisation agents should be as fine grained as possible. However, flowability is reduced with very fine grains therefore it is necessary to find an optimum between efficiency and conveying ability. A typical grain size distribution is shown in figure 2.

Compared to the feathery structure of lime, calcium carbide has a tetragonal crystal lattice and crushes in a sharp-edged way, therefore, conditioning of calcium carbide with auxiliary flow materials is generally unnecessary. In order to receive the best flow characteristics a fluxing agent is generally added during the grinding operation, thus pneumatic transport during injection does not pose any problems.

Calcium carbide is rarely used in its pure condition; mostly as mixtures of several components. Since all components have a similar density and are ground together with the calcium carbide, segregation can largely be excluded so that the desulphurisation effect is effectively constant during injection.

Calcium carbide is a hazardous material and reacts with water to form acetylene, a combustible gas. By adding coals with a high proportion of volatile components, carbide-based desulphurisation agents are possibly pyrophoric. For these reasons carbide mixtures must be stored in a dry place and under nitrogen. At temperatures over 700°C and in the presence of nitrogen, calcium cyanamide arises. This, so-called azotation reaction, is exothermic and localised heating can be enough to start the process. To avoid this modern hot metal desulphurisation plants are equipped with argon purging facilities.

During injection calcium carbide splits into calcium and carbon. The carbon separates as kish graphite into the slag and increases its viscosity so, in order to minimise the iron losses - which are typically 18 kg/t of hot metal - fluxing agents can be added to the calcium carbide. The first tests with fluxing agents used soda and fluorspar; later, several other alkali fluorides were added. By adding potassium cryolite, very good results can be obtained with regard to reduced iron losses. The

eutectic composition of potassium cryolite has approximately 45 % AlF_3 (See figure 3), and a typical composition is shown in figure 4.

Tests have shown that the optimum is 2 - 3.5 % potassium cryolite in the carbide mixture. This is a compromise between the desulphurisation effect, which decreases with increasing fluxing agent content and the lowest possible iron losses. Owing to the low melting point of approximately 600°C, potassium cryolite of eutectic composition is liquid at hot metal temperature and it has, therefore, optimum effectiveness. The viscosity of the slag is drastically reduced and the iron droplets which have been catapulted in the slag during the desulphurisation treatment can fall back into the iron bath. Thus, it is possible to halve the iron losses compared to the standard carbide - typically 7 kg of iron loss per tonne of hot metal. In a 4mtpa steel works, this corresponds to annual savings of approximately 40,000t of hot metal.

The use of fluxing agents does, unfortunately, carry some disadvantages. These substances, mostly based on fluorides, decompose during contact with hot metal, and with silicon they can form silicon tetrafluoride, SiF_4 , a gaseous, corrosive substance which leads to corrosion in the fume exhaust system. The use of alkalis as fluxing agents also means that contact with water on the slag dump will result in formation of heavy metal-rich eluted water. Thus, considerable environmental problems can arise.

During the 1980s, studies regarding the effectiveness of calcium carbide with a eutectic composition of approximately 70% CaC_2 , 30% CaO were conducted which, however, have not been pursued further. The reasons are; on the one hand, calcium carbide which is produced with this composition is difficult to process because the crystalline structure changes considerably, and the carbide is difficult to crush. On the other hand, the immersion depth of the desulphurisation lance and, thus, the residence time of the desulphurisation agent with the ladle desulphurisation, is higher than with the torpedo desulphurisation, so that a positive effect on the desulphurisation caused by the higher number of crystallisation cells in the eutectic carbide is not ascertainable.

In contrast to lime, calcium carbide mixtures are hazardous substances and are subject to the dangerous goods regulations. This involves the need for a considerable number of safety devices. Modern desulphurisation plants are, therefore, equipped with measuring facilities for determining the acetylene, oxygen and moisture content in the silo system as well as with the ability to purge with argon.

The production of calcium carbide is energy intensive, hence, due to significantly increased raw material and

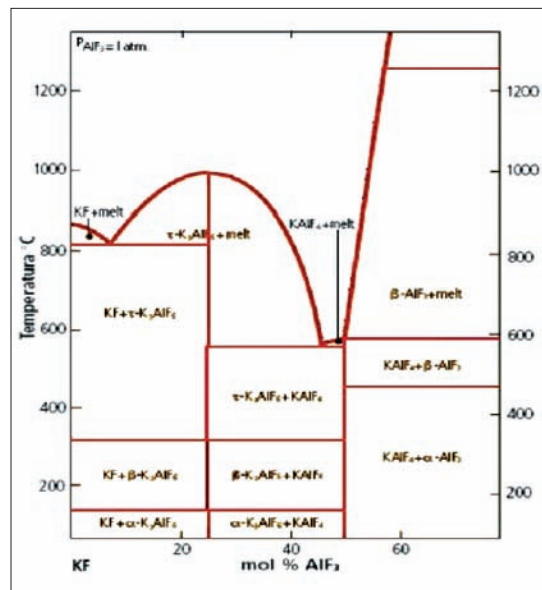


Fig.3 The KF- AlF_3 binary system

energy costs, calcium carbide has become less cost effective, being replaced in favour of magnesium.

MAGNESIUM

The use of magnesium for hot metal desulphurisation has increased significantly in recent years resulting from the considerable increase of high grade steel production and the good cost-performance ratio of the process (see figure 5). Some early uses of Mg for desulphurisation in the 1960s and 1970s included Mg-impregnated coke and Mg-lime briquettes but these have been superseded by Mg injection which is more controllable and efficient.

Magnesium is mainly produced by the Pidgeon process whereby magnesium oxide is reduced with ferrosilicon and coke in a metallo-thermic process. For use in desulphurisation, production via electrolysis would be too expensive. The magnesium vapour arising in this process is condensed, and the magnesium poured to ingots. Following machining by means of several cutting and milling units, granules arise which are screened above 200µm for safety reasons. For metallurgical and plant-specific reasons, the size granulation is limited to 1000µm maximum.

With the closure in recent years of European plants, a large part of the magnesium which is used for hot metal desulphurisation today comes from China. Additional raw material for Mg production is Mg alloy scrap (mainly AZ91 and AM50) from machining processes used in cars and aerospace. This type of magnesium is then remelted into ingots or directly machined into Mg powder for use in injection.

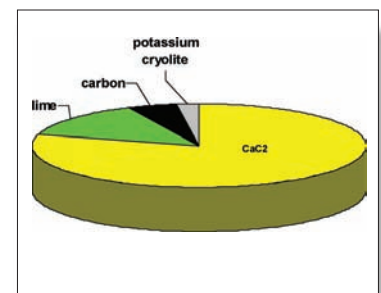


Fig.4 Composition of a typical calcium carbide-based desulphurisation agent with potassium cryolite as a fluxing agent

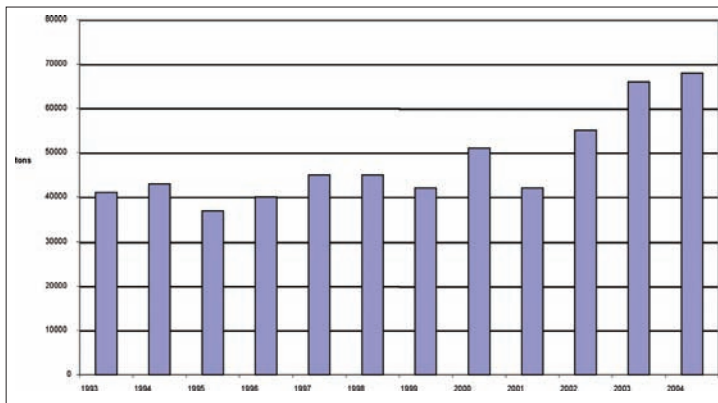


Fig.5 Worldwide Mg consumption for HM desulphurisation

In table 2, the classification of the scrap is shown. The higher quality scrap, classes 1 - 3 are mainly used for the production of desulphurisation agents.

The importance of magnesium as a constructional material has clearly increased over recent years thus the availability of primary material for desulphurisation has also increased. At first glance, magnesium is an expensive desulphurisation agent, however, if its effectiveness is taken into consideration - which is about seven times higher than that of calcium carbide - the specific desulphurisation costs are clearly lower than other desulphurisation agents.

Modern plants mainly desulphurise in the transfer ladle where the temperatures are about 100°C lower than in torpedo ladles. Since magnesium has a higher effectiveness at low temperatures, it is particularly suitable for this process. Although there are a few desulphurisation plants which only work with magnesium, without any additional desulphurisation agent, mainly co-injection plants are used which - apart from magnesium - also inject lime or calcium carbide. The reason is that, in contrast to the other typical hot metal desulphurisation agents, magnesium is a metal with high vapour pressure which can cause excessive ejections at high feed rate owing to the sudden vapourisation of the magnesium. The high vapour pressure also dampens the desulphurisation effect of primary magnesium when used in torpedo desulphurisation plants.

It has emerged that granules of magnesium alloys are preferred to granules of primary magnesium. The main alloying elements are aluminium, silicon, manganese and zinc. The vapourisation point of magnesium alloys is higher than primary magnesium, thus the magnesium component remains liquid and hence chemically active for a longer time. Also, the ejection tendency decreases so that the desulphurisation reaction with lime-magnesium mixtures takes place as smoothly as with calcium carbide mixtures. The usual segregation tendency of magnesium mixtures is also slightly reduced

Scrap class	Description	Example
1	Oil-free, clean and classified scrap	Waste parts from the die casting industry
2	Oil-free scrap with admixtures of escort substances	Oiled bosses incl. filter, composite material with steel
3	Scrap of classes 1 and 2, but containing oil or painted	Die casting parts
4	Magnesium powder and chips processing	Chips from die castings
5	All other scrap	Oiled chips

Table 2 Classification of scrap containing Mg

by the typical irregular grain shape of the granules made of magnesium alloys so that mixtures with a magnesium proportion of up to 25% can be satisfactorily injected.

In several steel works, mixtures of calcium carbide and magnesium are used as a desulphurisation agent. These mixtures have a magnesium content which is mostly between 10 and 20%. The advantage of these mixtures is mainly the lower investment in the plant engineering required because a mono-injection plant is sufficient, rather than the need for multiple injectors for different materials. The reactivity of desulphurisation can be controlled via the magnesium content. Thus, it is possible to save treatment time so that these desulphurisation reagents offer a possibility, without further investing in plant engineering, to treat hot metal reliably and efficiently.

FUTURE PROSPECTS

Hot metal desulphurisation will remain the most cost-efficient route for sulphur removal in steel production. According to the current level of knowledge the types of desulphurisation agent will not change, however, the relative use of each reagent will change as steel product demands change. Alternative processes such as use of calcium aluminate slag will probably not become accepted in the future owing to their high energy demand. The use of fluxing agents for reducing the iron losses will mainly increase in calcium carbide mixtures.

Due to its high efficiency magnesium will continue to be a major reagent, and further developments using Mg with secondary raw materials are expected. Lime will keep its current importance as a desulphurisation agent, and methods for the utilisation of work-generated calcareous residuals will definitely increase.

Wolfgang Gitterle is Director of Sales & Marketing at Almamet, Ainning, Germany

CONTACT: gitterle@almamet.com