Desulphurization of pig iron using calcium carbide based reagents

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Use of calcium carbide based reagents is a long established practice for the desulphurization of pig iron/hot metal resulting in the removal of the sulphur from the molten metal as calcium sulphide into the slag floating on the molten metal surface.

At SA Calcium Carbide desulphurizer reagents are produced by blending calcium carbide with various other additives and milling the mix to a fine powder with a particle size of approximately 95% smaller than 75 microns.

This paper discusses factors such as ladle design, injection system and lances, gas and solid flow rates, sulphur levels, reagents, temperature and slag affecting the desulphurization. Also included is discussion on iron losses and reduction of iron loss. The last section is allocated to safety requirements for calcium carbide based reagent, dealing with spillage and fire as well as transportation, transfer, handling and storage.

Introduction

SA Calcium Carbide has been making calcium carbide desulphurizer mixtures for 30 years and has extensive experience in the use and application of this material.

Calcium Carbide is produced at the Newcastle site in a 50 MW submerged arc furnace using calcium oxide and carbon and electricity, the reaction is $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$ (Figures 1 and 2).

Ladle design

The design of the ladle is important, especially the depth of injection in order to maximize the reaction time for the reagents. The surface area should be minimized to avoid heat loss and air exposure, and a hood is often used for this and to prevent splashing from the ladle on to adjacent structures during reagent injection.

The pouring lip design is important to assist in deslagging and to reduce iron loss as is the freeboard of the ladle to avoid splashing losses. As can be seen, it is important to design the desulphurization treatment ladle to meet the plant throughput rate especially to injection depth, circulation/mixing and possible splashing of hot metal.

Injection system and lances

The design of the injection system is also important, pressure vessels with a steep sided cone, fitted with a fluidization cone or nozzles at the bottom to assist with an even continuous flow of reagent into the nitrogen carrier gas stream. In treatment ladles normally a refractory coated lance is lowered vertically into the molten iron to within 500 mm of the ladle bottom to maximize the injection depth. Co-injection systems are available for injecting more than one reagent simultaneously into the hot metal.

Different lances are available—original straight bottom discharge, T- lance with the discharge from 2 holes on the side of the lance parallel to the ladle bottom, 4 hole lance
and dual pipe lances have all been tried. Their use is dependent on the individual customer’s system. Lance life is mostly a function of heat stresses and cooling, and shorter injection times increases lance life. Improved refractory designs with lower conductivity, increasing the thickness and addition of stainless steel fibres to the refractory covering on the lance have extended lance life. Cleaning of the lance outlets, especially on multi port lances, improves lance life by reducing clogging.\textsuperscript{1,2}

The ladle side plug injection system has been tried and while good desulphurization and efficiencies were obtained, the cost of the side plug was expensive. Renewing the side plug was also time consuming together with the added risk of burn-through at the bottom of the ladle.

It is important to get a smooth constant flow of reagent to prevent lance clogging and achieve good desulphurization efficiency. This is achieved by the control of the top pressure in the injection vessel, the fluidization cone gas flow and the main carrier gas flow. Bends in conveying pipe work should be kept at a minimum and where required long radius bends should be used. Computerized control of the whole injection system from lowering and raising the lance to control of gas pressure and gas and reagent flow has improved the desulphurization process. More consistent final sulphurs and improved reagent efficiencies are achieved.\textsuperscript{3} (Figure 3.)

**Gas and solid flow rate**

The position of calcium carbide particles relative to the gas bubbles or in the molten iron strongly influences the desulphurization efficiency. Particles on the surface of gas bubbles are able to make contact with sulphur in iron while those others in the bubble will not, unless they are able to reach the interface. Calcium carbide particles which enter directly into the liquid iron travel more slowly to the Iron slag interface than the particles in the bubbles and have a longer residence time, increasing the reaction with the sulphur in the iron. Plume reactions depend heavily on the injection conditions and the gas to solids ratio. The rising bubbles cause the agitation, circulation and mixing of the iron. (Figure 4.)

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**Figure 3. Flow diagram of a typical injection unit**

Legend: 1 – Ladle; 2 – Ladle cover; 3 – Lance; 4 – Lance support unit; 5 – Transfer pipe; 6 – Desulphurizer storage and weighing

**Figure 4. Flow dynamics in the nitrogen/calcium carbide plume**
An increase in the gas flow increases the velocity of the rising plume and reduces the residence time of the particles in direct contact with the iron thus, decreasing the desulphurization efficiency of these particles. Increased gas flow gives more and larger bubbles which creates a greater surface area for more particles to make contact with the molten iron. Increasing the solids flow rate increases the number of particles inside the bubbles and makes it difficult for particles to reach the bubble surface. It can be clearly seen that it is essential to optimize the gas to solids ratio to achieve the best desulphurization efficiency within time constraints and process requirements. The circulation of the molten iron is beneficial, as this enables sulphur in the iron to also contact and react with calcium carbide and lime particles that have risen through the iron and are sited at the iron-slag interface.\(^4,5\)

In many of the open ladle injection systems with a single bottom outlet lance the carrier gas flow was of the order of 600 N litres/minute and reagent flow of approximately 60 kg/minute giving a gas to solids ratio of 10:1. It is my opinion that this needs to be optimized for each system. Higher gas velocities assist in preventing lance clogging, while lower flow rates of reagent have been found to result in better desulphurization efficiencies. Rates of the order of 35 kg/minute for carbide based reagents appear to be preferred where the available treatment time allows. The multi-port lances like the T lances with two outlets allow for higher gas flows and, as this splits the reagent flow, it can give better efficiencies.

**Sulphur levels**

The sulphur in the molten iron from a blast furnace operation or TiO\(_2\)-FeO separation in the case of ilmenite treatment is influenced by the sulphur level in the reducant used in the process. Desulphurizer reagent usage increases as the initial sulphur level increases, but also increases exponentially as the final sulphur level aimed for decreases. Obviously the initial and final sulphur levels then influence the treatment time. Reducing conditions in the molten iron are necessary for effective desulphurization.

Initially on injecting calcium carbide based reagents any oxygen activity in the iron e.g. metal oxides, has to be reduced.

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C + O = CO
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Some basic slag containing calcium carbide and lime also needs to be present to trap the calcium sulphide rising to the surface of the molten iron. In the case of the ilmenite process there is little slag so the incubation period should be short.

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CaC_2 + S = CaS + 2C
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CaC_2 + O = CaO + 2C
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**Reagents**

The particle sizing of the desulphurizer reagents is important to increase the particle surface area of reagent available for contact with sulphur and reduce the thickness of the calcium sulphide on the particles. This makes diffusion of sulphur through this layer to the calcium carbide easier. To achieve suitable particle sizing of less than 75 microns, at SA Calcium Carbide, the calcium carbide and other additives are blended together in a computer controlled batch weighing system and milled in a large combination rod and ball mill. (Figure 5.)

Addition of dolomite to the calcium carbide based reagents assists with making more bubble surface area available so reagent particles can contact the iron. It also increases the agitation and mixing and helps to disperse more particles directly into the molten iron. Assuming 0.6 Nm\(^3\)/minute of nitrogen carrier gas, the decomposition of the dolomite to release CO\(_2\) on contact with the hot molten iron adds considerably to the agitation in the treatment ladle.

**Temperature and slag affecting desulphurization**

While desulphurization can still be achieved with iron temperatures of slightly below 1300\(^\circ\)C, temperatures of 1350\(^\circ\)C give better desulphurization and reagent efficiencies. The higher temperatures also reduce the slag viscosity with a reduction of iron trapped in the slag. If the slag contains significant levels of metal oxide, the calcium carbide can react with the oxygen in the oxide first, reducing the reagent efficiency and this should be compensated for.

**Reduction of iron loss**

The main sources of iron losses in the desulphurization operation are pig iron granules trapped in the slag on top of the molten iron, splashing during injection of reagent, loss during deslagging operations and skulling on the ladle refractory sides.

The Marangoni effect causes iron droplets to be propelled into the slag where they cannot continue to coagulate and are caught in the rigid net shape desulphurization slag instead of falling back into the molten iron. Granules are finely distributed and cannot be removed due to a high degree of intergrowth. The pig iron cools during the desulphurization operation, causing some of the dissolved carbon to drop out. This together with the carbon released from the reaction of sulphur with the calcium carbide is incorporated into the slag increasing its viscosity. It is then more difficult for the iron droplets to leave the slag back

![Figure 5. Combination rod and ball mill for producing various calcium carbide based desulphurizer mixtures](image-url)
into the pig iron. Formation of di-basic calcium silicate together with the carbon (graphite) increases the viscosity and gives the slag its crumbly appearance. Chemical fluxes are the most effective way of reducing iron loss via the slag. Fluoride based fluxes such as fluorspar and cryolite are most commonly used while soda ash on its own or with the fluoride fluxes has been used. While these fluxes reduce the viscosity of the slag and thus the iron loss, a higher consumption of desulphurizer reagent is required to achieve the same desulphurization level (1% flux can increase reagent required by up to 3%). Thus for any operation the amount of flux and the reduction in iron loss needs to be traded against the increase in desulphurization reagent. Addition of approximately 3% flux appears to be commonly used. Alkaline silicates such as nepheline syenite are reported as having been successfully used with an improvement in desulphurization and reduction in iron loss.

The turbulence of the injection is influenced by the carrier gas flow and the rate of desulphurizer reagent injection. Carrier gas and the volume of gas released by decomposition of or volatilization of components of the reagent needs to be controlled to avoid splashing of molten iron from the treatment ladle. The free board chosen in the ladle design is also important to limit loss due to splashing. The deslagging operation, on completion of treatment of the pig iron, needs to be carefully controlled to avoid unnecessary losses. Design of the ladle pouring spout is important to prevent run out of the molten iron during the raking process of deslagging. Tilting of the ladle during deslagging should be adjusted at different stages to reduce loss of molten iron. Use of a porous plug with a nitrogen flow to push the slag forward towards the spout reduces the required number of deslagging strokes and thus the loss of iron. (Figure 6.)

The lower the temperature of the slag, the higher the viscosity and the higher the iron loss will be. Also the more slag created during the injection of reagents in the treatment of the iron and together with any initial slag, the higher the iron loss will be.

Safety requirements

The calcium carbide on its own is not hazardous but reaction of the calcium carbide with moisture from any source releases acetylene which presents a serious hazard of fire and/or explosions. If contact of the calcium carbide based desulphurizer with moisture is avoided the material is safe to handle. To reduce the risk, nitrogen with a dew point of -40°C or lower is used in blanketing of material stored in silos and for conveying reagent. This blanket excludes moisture and reduces oxygen levels below the lower explosive limit for acetylene (LEL is approximately 2% acetylene in presence of > 6% oxygen).

Handling and storage

Offloading areas and storage silos must obviously be designed to prevent contact of desulphurizer reagent with rain and other moisture sources. Storage silos should have a constant nitrogen purge to prevent ingress of moist air through a bag filter due to atmospheric temperature fluctuations. Gas analysers should be installed to monitor acetylene and oxygen levels in storage vessels. This then enables nitrogen purging to be adjusted to keep the acetylene and oxygen levels at acceptable concentrations (SA Calcium Carbide believe acceptable levels to be < 0.3% acetylene and < 2% oxygen). Storage silos and vessels should have a steep sided cone shape with a fluidizing ring in the bottom to ensure free flow of material out the bottom. Desulphurizer is like all fine powders which can compact on standing, especially if vibration is present.

Transportation and transfer

Transportation of desulphurizer must meet the laid down requirements for the transportation of hazardous substances by road. The drivers of road tankers must have a valid Hazchem drivers licence and should be trained in the specific hazards of the material being transported. The tanker must have Hazchem stickers, in this case for calcium carbide, a blue diamond indicating ‘dangerous when wet’ and emergency assistance numbers. In the cabin of the vehicle there must be a TREM card available, giving information on hazards of the product and information on handling of incidents. (Figures 7 and 8.)

![Figure 6. Schematic of ladle deslagging](image)

![Figure 7. Example of a pressurized tanker for safe transportation of desulphurizer mixtures](image)
Carbide based desulphurizer must be transported under a nitrogen blanket with the tanker gas space pressurized to 100 kpa pressure. Mounting of nitrogen cylinders as an emergency back up on the tanker is advisable. On arrival at the customer site the gas space should be tested to ensure the acetylene (< 0.3%) and oxygen (2%) are at acceptable levels before proceeding with offloading of the material. If acetylene and /or oxygen levels are high or the pressure on the tanker is low, purging with nitrogen should be carried out to ensure safe gas levels for offloading.

Nitrogen should be used as the pressurizing and carrier gas for transferring the desulphurizer from the tanker to the Storage silo. An emergency stop, on the nitrogen supply to the tanker, is required in case of an incident during offloading to minimize any spillage. It is also advisable to fit a remotely operated valve on the Tanker outlet pipe to immediately stop the flow of material. The valve must be situated before the connection to the offloading flexible and be operated from the pneumatics of the tanker or some suitable supply of air or nitrogen from the plant. (Figures 9 and 10.)

**Spillage and fire**

In case of spillage, prevent contact of the material with moisture as far as possible. If dry conditions exist and there is no reaction of the calcium carbide with moisture the material can be recovered by sweeping up into dry metal containers.

Desulphurizer mixtures can, in contact with sufficient moisture, generate enough heat to spontaneously ignite any acetylene produced. In case of a fire, remove all ignition sources, and move personnel upwind. Allow the fire to burn itself out and only use dry powder extinguishers where equipment or buildings are on fire or there is an imminent danger of catching fire. Beware of areas where the dry powder has been used on top of the desulphurizer as if there is still moisture present, flames might suddenly erupt from under the powder layer. When the flames have stopped and the material is possibly glowing red, if deemed safe, a long handled flat metal rake could be used to separate glowing material from dry unreacted material. Persons should be trained to deal with spillages and fire and the assistance of the supplier sought if required. Disposal of residues should be undertaken with care with the assistance of knowledgeable and trained personnel.

**References**


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Born in Pietermaritzburg and graduated with a BSc Hons. At Natal University (Pietermaritzburg Campus) in 1963. Worked in Bulawayo Zimbabwe for 14 years before returning to South Africa, in 1978, to the Calcium Carbide business at Ballengeich, Newcastle KZN. Held various positions during his stay, including Laboratory Manager, Production Manager and Technical Manager during the 30 years in the carbide business. In June 2008 he retired and is currently employed on an ad hoc basis as a Consultant for SA Calcium Carbide.