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CO_2 Problems and waste recycling. Research at the Institute of ferrous metallurgy[(•)]

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Abstract In a short introduction tests and calculations about CO_2-ice-blocs in the deep sea, use of CO_2 for underground-coal-gasification and tertiary processes to increase oil-production by CO_2-flooding are shown. New activities are presented e.g. CO_2-injection into EAF combined with injection of coal, coke or directreduction-fines. After research of injection of coals, fine ores or dust into blast furnaces and other shaft furnaces activities are compared with injection of hot reducing gas generated by coal or waste gasification or top gas recycling combined with injection of fine solid fuels. Results of injection of prepared plastics (Duales System Deutschland), shredder-light-fraction from car-recycling and unburned carbon of power-station-ashes are discussed. Beside production of direct-reduced-iron by H_2 fluidized reactor results of the reduction behavior ore/coal or dust/coal pellets or briquettes for the use in rotary hearth or modern shaft furnaces are shown.

Keywords CO_2 Emission and Injection. Wastes Recycling. Shaft Furnaces. Direct and Smelting Reduction. Steelmaking.

Problemas de CO_2 y reciclado de residuos. Investigación en el Instituto Siderúrgico

Resumen En una breve introducción se describen las pruebas y cálculos referentes a bloques de hielo de CO_2 en el mar profundo, el uso del CO_2 para la gasificación de carbón subterráneo y procesos terciarios para aumentar la producción de aceite por medio del torrente de CO_2. Dentro de las nuevas actividades se presentan, por ejemplo, la inyección de CO_2 en el horno eléctrico de arco (HEA) combinado con la inyección de carbón, coque o de finos de los procesos de reducción directa. Después de la investigación de la inyección de carbones, se comparan, por un lado, la inyección de los minerales finos o polvos en los hornos altos y otras actividades en los hornos de cuba con la inyección del gas reductor caliente generado por la gasificación del carbón o de los residuos o reciclado del gas del tragante combinado con la inyección de finos de combustibles sólidos. En el presente trabajo se discuten los resultados de la inyección de los plásticos preparados (Sistema Dual Alemán), de la separación de fracciones ligeras del reciclado de autos y de carbon no reaccionado de cenizas de la estación de poder. En el área de la producción de hierro reducido directamente en el reactor de lecho fluidizado de H_2, son mostrados los resultados del comportamiento de la reducción de mineral con carbón o pellets de polvo con carbón o briquetas para el uso en el horno rotatorio o en modernos hornos de cuba.

Palabras clave Inyección y emisión de CO_2. Reciclado de residuos. Hornos de cuba. Reducción directa y reducción *flash*. Producción de acero.

1. INTRODUCTION

In 1982 a thesis was finished in the department of Metallurgy at the RWTH-Aachen to decrease the CO_2-emission after combustion of fossil fuels. The source and decrease of CO_2, the greenhouse-effect and the influence of the steel industry was discussed. Furthermore the circulation of CO_2 was shown; the possibility to bring the CO_2 as dry-CO_2-ice blocks in the deep see seemed to be an

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interesting way. Industrial produced CO_2-ice has a density of 1.4-1.6×10^3 kg/m^3 and is heavier than water. In tests the sublimation of CO_2-ice in salt-water was measured and concluded that CO_2-ice-blocks would get a small shell of water-ice but the sublimation of CO_2 will be very slow[1].

In a project a combined steam-CO_2-injection to foam was discussed to increase of flooding efficiency of tertiar crude oil production by simulation in an autoclave. This foam was used to increase the oil-production; by pressing out sticky oil with hot water often happened an "overriding" of the watersteam and the oil remained in the earth. By foam this overriding was blocked and the oil could be pressed out; CO_2 was a suitable gas for the foam formation and also made the oil less sticky[2-4].

To gasify coal beside with air, oxygen and water-steam the influence of CO_2 was studied in the High Temperature-Fluidized-Bed-Reactor, see figure 1[5-8].

Also in the field of Underground-Coal-Gasification CO_2 was used in research projects; on the one hand the reactions of gasification were influenced on the other side a lot of CO_2 was thought to remain under ground, see figure 2[9-14].

Parallel to these research activities special subjects in the field of metallurgy of iron and steel were investigated. Aichinger gave in 1991 the development of the specific CO_2-emission of the steel industry[15].

Ameling showed that to bring down the CO_2-output by different ways was more interesting in the following years than the use of CO_2, see figure 3[16].

2. EXAMPLES OF RESEARCH

In the following some subjects are stressed:

2.1. Fine and CO_2 –Injection into Electric Arc Furnace (EAF)

Beside different theses on EAF[17-22], Wirjomiyoyo[23 y 24] showed in the abstract of his thesis that the CO_2-emission from steel-making depends on the use of energy sources and reduction

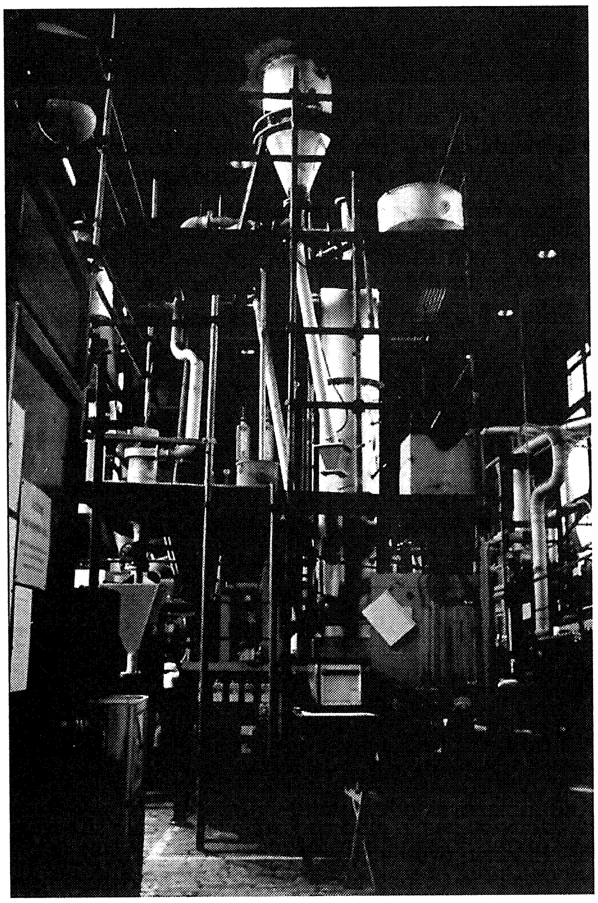

Figure 1. High-Temperature-Winkler(HTW) Gasifier.

Figura 1. Gasificador de alta temperatura Winkler.

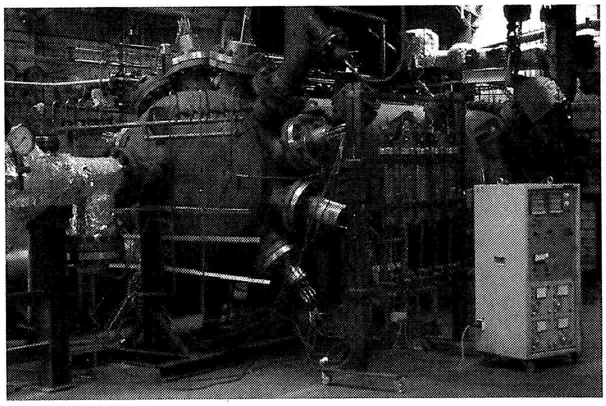

Figure 2. Underground coal gasifier (Autoclave).

Figura 2. Gasificación subterránea de carbón (autoclave).

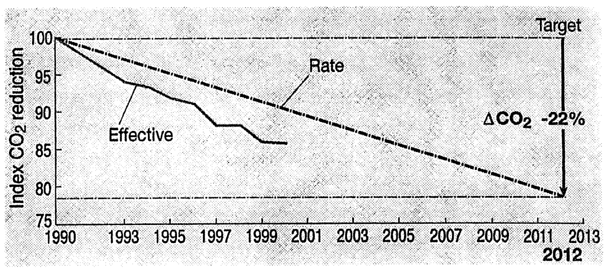

Figure 3. Development of CO_2 monitoring in the steel industry[16].

Figura 3. Evolución del CO_2 medido en la industria del acero [16].

agents; the discussion of CO_2-emission as a global problem lead the world steel industry into this important subject.

The problems of waste and rest fines materials as well as modeling of EAF process should be considered, too[25]. The land filling or fines stocking are well known problems in steel industry. The fines generation is unavoidable due to material handling and degradation during the process. On the other side, the problems of dust and sludge generation must taken into the consideration.

The initial observation were done by thermodynamic calculations as well as ChemSage simulation and literature research conclusions. The industrial experiences from steel-making by different ways to produce steel, for examples through LD-converter, secondary metallurgy and electric arc furnace showed no disadvantages by its processing with CO_2 and fines material. By experimental tests in the steelworks at Krakatau-Steel in Indonesia and in Institute for Ferrous Metallurgy RWTH Aachen, it was concluded that the overall performance of electric arc furnace can be increased by injection of CO_2 and fines material.

The cost of energy is one of factors for the selection of steel-making routes. Beside steel also gas, slag, dust and sludge are produced, too. As an exhaust gas CO_2-emission depends on the input of energy source and reduction agent in the process of steel-making.

In some of the direct reduction processes like HyL-III, Finmet and Iron Carbide CO_2 will be blown continuously from its separation of the reduction gas cycle. Some alternative solutions like CO_2 recovery from exhaust gas and permanent isolation were suggested to reduce the emission.

On the other side the steel industry is facing a problem of fines generation and its handling. The fines generation in form of dust as well as small size material fraction is unavoidable due to its handling and the process itself. As the world steel production increases, the use of raw material is also increased as well as its handling and processing. Consequently the amount of generated fines is also increasing. The same case occurs also by direct reduced iron (DRI), coke and sinter production. Furthermore the problems of dust and sludge from the steelworks must be considered.

The industrial experiences of using CO_2 and fines for steel-making were shown:

The initial observation are first done by thermodynamic calculation as well as ChemSage simulation in the Institute for Ferrous Metallurgy, RWTH Aachen. The simulation shows that the feasibility to use CO_2 and fines for steel production thermodynamically can be answered. In the case of injection into EAF, simultaneous decarburization and physically evidences of slag foaming by CO-gas generation in the steel melt were investigated. The industrial as well as laboratory experiments were conducted to analyze the influence on metallurgy as well as energy saving by CO_2 and fines injection. The industrial experiments conducted in the steel works of PT Krakatau Steel(PTKS), Indonesia, were divided two parts of experimental stages.

In the first stage, CO_2 and DRI fines were injected into a 2 ton EAF. The results showed that due to the injection of CO_2 and fines, the built up of foaming slag were accelerated. The melting energy was influenced by the generation of CO gas as well as slag foaming. The overall results of experiments in the 2 ton EAF showed that no difficulties are found due to the facts that fines DRI can be injected easily with CO_2 acted as carrier gas into EAF. The foamed slag, decarburization and saved electric energy were measured. The safety aspect were discussed, the amount of generated CO gas will be directly burned as post combustion in EAF.

After the reviewed first stage results, the second stage experiment were arranged in the 120 ton EAF of Slab Steel Plant PTKS, see figure 4. In this case, around 22000 Nm^3/h CO_2 were blown from HyL-III direct reduction plant from the separation continuously in the reduction gas circuit. The fines DRI are produced approx. 450 t/d from both HyL-

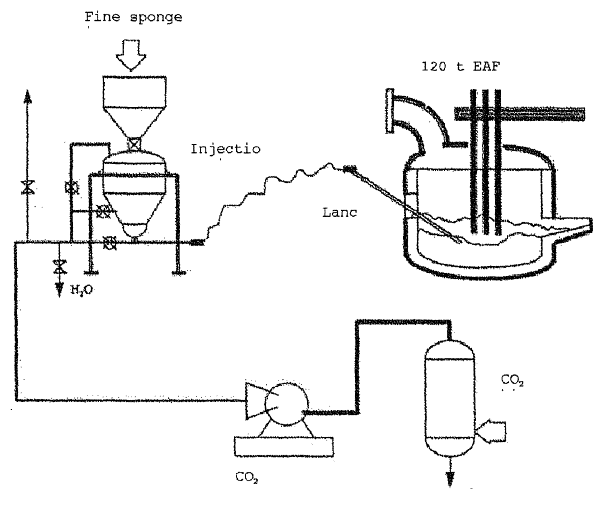

Figure 4. 120 t EAF at Krakatau Steel[23].

Figura 4. 120t HEA en Krakatau Steel[23].

I and HyL-III direct reduction plant. In this project, the injection of fines DRI as additional charge material for EAF was initiated. The results brought furthermore the advantages of the gas injection as stirring energy for a better metallurgical process in EAF.

The laboratory experiments were introduced to explore details of the results of the industrial experiments. A laboratory scale of EAF was developed and constructed in Institute for Ferrous Metallurgy, RWTH Aachen.

The furnace was constructed with a furnace vessel and a roof; it was equipped with a 9.7 kVA DC source, a electronic control of the graphite electrode, injection equipment, computerized process data acquisition and online temperature measurement. The melt capacity is approx. 5 kg, see figure 5.

CO_2 under normal condition as a gas molecule has a high stability and usually is used as inert gas. CO_2 will be dissociated in to CO and Oxygen at high temperature, by ultra violet and also by electrochemistry reaction e.g. slag-gas boundary reaction. At steel melt temperature of 1600°C, CO_2 should be dissociated approx. 0.05%. At the first stage laboratory experiments the fundamental facts showed that the dissociation of CO_2 was clearly determined by observation of increased oxygen dissolution in the steel melt.

The generated CO was also observed in the industrial experiments and was directly burned as part of the post combustion process in EAF. The influence of the different injected gases like argon, air and CO_2 was measured.

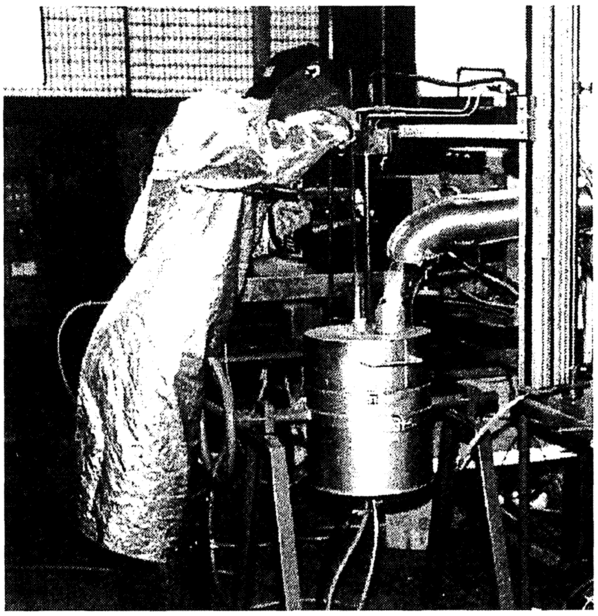

Figure 5. Pilot furnace at Institute, RWTH Aachen[23 y 24].

Figura 5. Horno experimental en el instituto, RWTH Aachen[23 and 24].

By CO_2-injection a decarburization takes place and the CO-amount increases together with a slag foaming. Adding of carbon can stop the decarburization and the Fe- fines injection increases the steel amount.

As conclusion it was stressed that steel industry produces not only steel but also emission, dust and fines. An alternative method of solving fines- and dust-generation as well as CO_2-emission is the injecting into the steel bath of an EAF. The experiences of steel making as well as industrial and laboratory experiments showed a potential benefit of this method. The thermodynamic simulation and the experiment results showed that not only the metallurgical improvements were achieved but also the overall performance of EAF operation e.g. energy consumption can be improved accordingly.

2.2. Injection into High-Turbulence-Mixer (HTM)

This Mixer was developed to stir molten metals without injection of gases but by induction forces. Improved product quality can be achieved by the application of a number of metallurgical treatments at different stages in the iron- and steel-making route, each one tailored to match local conditions and taking best advantage of them. In this respect, the mixing of active substances such as slag, powders and gases with liquid metal is a very important and decisive step for desulphurization, deoxidation, degassing, as well as alloying and inclusion control. Furthermore dusts and wastes can be treated without any gas injection[26 y 27].

The high turbulence mixer (HTM) described enables easier mixing of different materials with molten metals involving minimum material loss. It is especially suitable for the mixing of granulated materials and substances in powder form. Due to its mixing ability, the HTM technology will speed up the processing rate by using it either batch-wise in small reactors or continuously. The HTM-reactor is a cylindrical lined vessel filled with liquid metal. The metal is stirred by inductive forces caused by the electromagnetic stirrer beside, see figure 6. Two waves are moving to the top of the vessel until they hit together and so a kind of vortex is created. The small batch-wise working reactor is able to treat one ton of liquid metal and is presently used in different foundries.

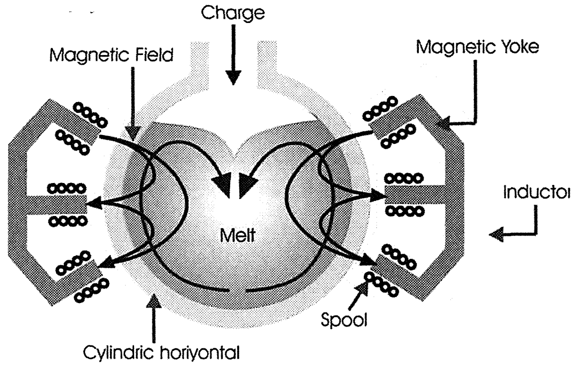

Figure 6. Principle of the HTM-Process[26].

Figura 6. Principio del proceso HTM [26].

In order to avoid heating losses of the melt the second continuous working version of the HTM was built in connection with an induction furnace to treat around 4.5 tons of liquid metal. Research tests under different mixing conditions are also done in this reactor on such material as shredder-light-fraction and pyrolytic coke[28], dusts[29], sponge iron[30] and additions.[31] In the HTM-reactor hot metal has been desulphurized intensively by addition of lime.[31] The process was also used successfully to produce nodular iron by addition of Mg with small losses by burning.[31] The behavior of Zn out of EAF-dust in the HTM is presented and discussed. The Results are shown in figure 7 [29]. Lead was treated in the same way with similar results.

In contrast to the behavior of zinc and lead which are evaporated, chromium and nickel coming from stainless steel dust are enriched in the iron bath. The produced slag does not cause problems when leaching tests are performed.

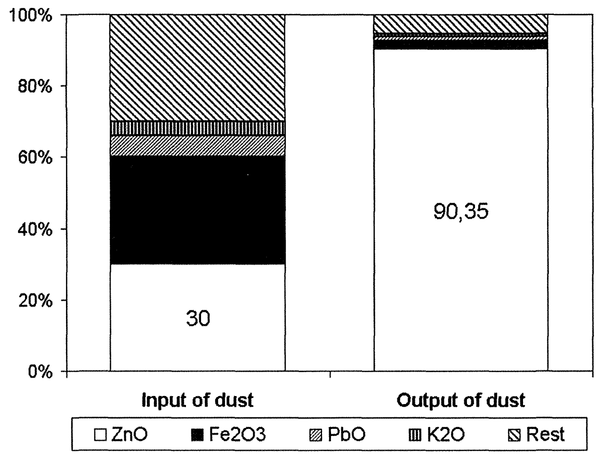

Figure 7. Composition of in- and outcoming Zn-dust[29].

Figura 7. Composición del polvo de zinc a la entrada y salida [29].

In special cases chromium and nickel can be defined as impurities; these elements can be removed separately by oxidation with iron ore and pure oxygen or diluted by addition of DRI [32]. Beside metallurgical tests research was done to improve the refractories and energy consumption[33].

2.3. Injection into shaft-furnace (blast furnace, cupola furnace and imperial smelter)

Within the last decades blast furnace productivity has steadily in creased and the total fuel consumption decreased. In order to minimize the input of coke its substitution with pulverized coal injection was started more intense in the early eighties[34-37].

At the Institute of Ferrous Metallurgy a laboratory rig was developed to investigate pulverized coal injection in detail. This rig simulates the behavior of fines injected into the raceway of the blast furnace[38-43]. The coal sample is blown by a shock wave into preheated gas with 1100°C (2012°F), simulating the hot blast, mixed with it and passed through a high temperature zone of 1700°C (3029°F), simulating the raceway. The combustion gases are analyzed to their contents of CO, CO_2, CH_4, H_2 and O_2 and the combustion degree is calculated.

While simulating blast furnace conditions the effect on the ignition and combustion behavior of different coals such as porosity, particle size, content of volatile matter, carbon and ash or injection rate could be tested. Further investigations were performed to analyze the effect of catalysts on coal conversion, oxygen enrichment of the hot blast, preheating of the injected coals or different lance geometries.

The results obtained have shown that they are transferable to the real blast furnace, for the test done parallel at the blast furnaces[44 y 45] to get more information e.g. about the raceway it was measured by advanced measuring methods like laser-technique[46], that the depth of the raceway was becoming shorter by injection of coal[47].

Also tests and discussion started to inject coal mixed with different fine materials. The reasons for a combined injection of coal and fine iron ore or iron containing dust are various, e.g. the amount of fine ore increases steadily due to a decreasing number of high-grade lump ores. The injection of fine iron ore to substitute pellets or sinter and herewith to reduce agglomeration and pig iron costs and energy[48].

For the different proposes the rig was steadily adjusted, the latest situation is shown figure 8.

It was found out that by using a coal with a low content of volatile matter the highest reduction degree was reached. The result shows that the reduction degree is dependent on the ignition and combustion behavior of the coal[49].

Further experiments were performed in order to analyze the effect of the particle size on the reduction degree.

The laboratory experiments have shown that a complete reduction of hematite iron ore to metallic iron is possible within the short residence time of 10-20 ms. Therefore further experiments were performed with blast furnace flue dust, steel plant residues and rolling mill scale. Concerning the iron and carbon content of these materials an injection into the blast furnace seems to be possible. Figure 9 shows the results of a combined injection of flue dust and coal.

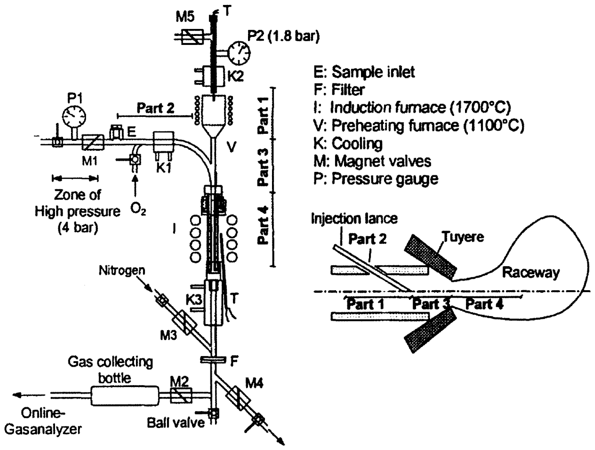

Figure 8. Modified injection rig[48 and 52].

Figura 8. Equipo modificado para la inyección [48 y 52].

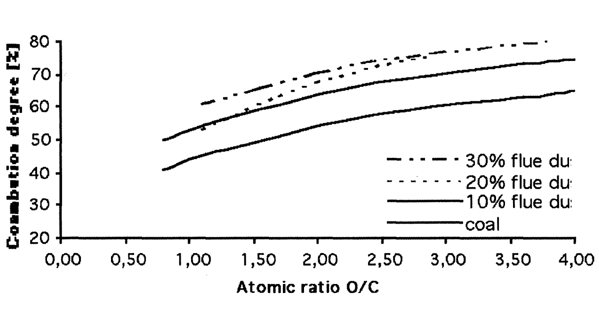

Figure 9. Combustion behavior of coal for different percentage of flue dust in the mixture[50].

Figura 9. Comportamiento en combustión del carbón para diversos porcentajes de polvo de tragante en la mezcla[50].

Further research about the racy way brought results and knowledge about different materials[50-52], e.g. pet coke, mill scale, BF-sludge, activated carbon and catalyst mostly as mixture with coals. Figure 10 shows the influence of mixtures of different coals and mixtures of waste with coal.

Beside injection of solid materials the recycling of treated BF-topgas or hot reduction gas produced in gasifier out of carbon, waste materials and biomass is researched[53]. It was found that these gases with oxygen and carbon are suitable to decrease the coke rate, to influence the gas flow and to minimize the CO_2 output[52 y 54-56].

Beside injection into blast furnace research was carried out to recycle foundry dusts into cupola furnace. The different circumstances in the tuyère level had to be studied and discussed[57].

It was possible to recycle different foundry dusts and furthermore e.g. plastic. It was found that no dioxin appeared in the off-gas[58 y 59].

To increase the injection rate of unburning material or new process was developed. Parallel to test at a cupola furnace an injection-coke-bed-simulator was built up at the institute, see figure 11. In this aggregate dusts are injected by a natural gas/ oxygen-burner. Aim of this research is to study the

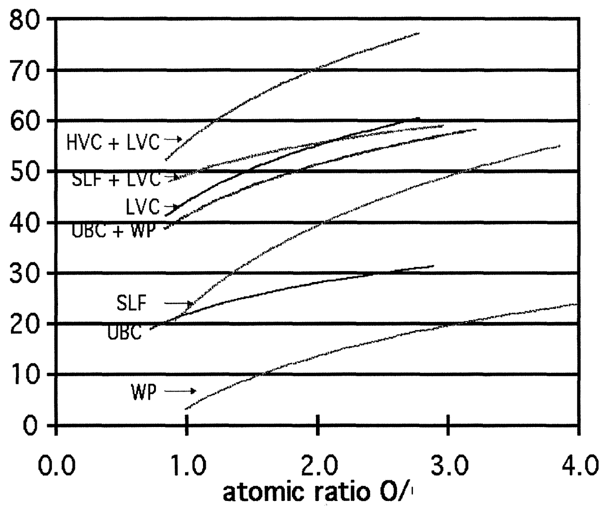

Figure 10. Combustion behavior of unburned carbon of power station (UBC) with and without waste plastics (WP), pulverized coal (HVC - high volatile coal; LVC - low volatile coal) and shredder light fractions (SLF=ASR ; automobile shredder residue) from car recycling.

Figura 10. Comportamiento en combustión del carbón que no ha reaccionado en la central térmica (UBC) con o sin residuos plásticos (WP), carbón pulverizado (HVC - carbón volátil alto; LVC - carbón volátil bajo) y fracciones ligeras de la separación (SLF= ASR; residuo de la separación del automóvil) en el reciclado del auto.

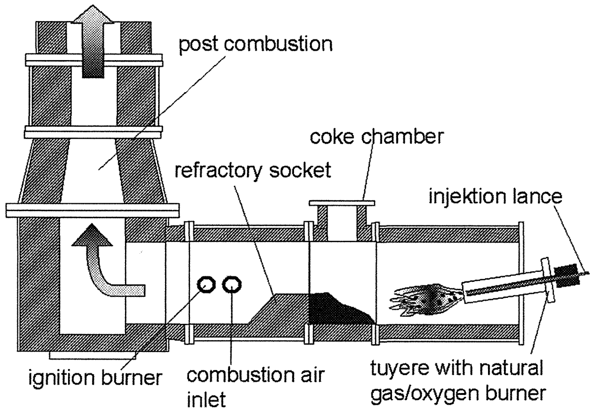

Figure 11. Injection coke-bed-simulator.

Figura 11. Simulador de la inyección en el lecho de coque.

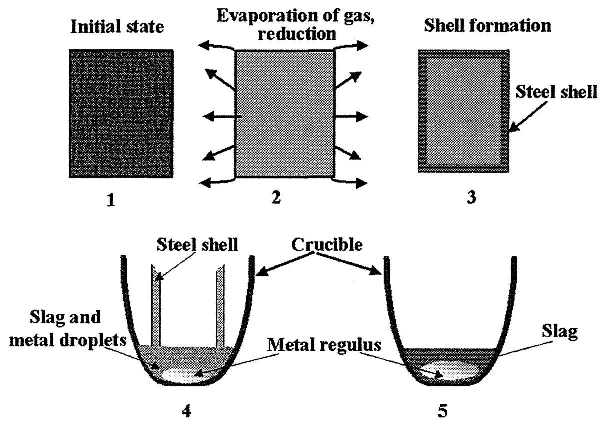

Figure 12. Reduction and smelting mechanism of briquettes with embedded carbon[71].

Figura 12. Mecanismo de la reducción y fusión de briquetas con carbón embebido [71].

behavior of such hot gas injection with dusts on the coke and in the furnace[60].

Furthermore dusts of a zinc-production were injected into an Imperial-smelter to recycle this waste[61].

2.4. Direct and smelting reduction

Research activities were carried out in rotary kilns to explain swelling, sticking and scaffold formation[62-65]. Beside reduction and smelting in shaft furnaces[66] the reduction behavior was studied in fluidized beds[67 y 68] including treatment of wastes[69] and with different gases[70].

The behavior of briquettes with embedded carbon and self-reducing pellets was investigated. Tests with briquetted dust from iron and steel industry were performed. The briquetting process and the reduction behavior of briquettes produced from different dusts, first bound by different binders and with different carbon contents were studied. Due to the fast reduction of the iron oxides at the outer part of the dust briquettes a steel shell was formed.

The increase of temperature to simulate the moving down in a shaft showed that the halfreduced material in the middle part of the briquette can be smelted[71].

Further increase of temperature causes collapse of that shell. Finally a completely separated slag and metal phase occurred, see figure 12. Based on the experience in laboratory tests industrials tests in the Hamborner Shaft Furnace “Oxicup” has been successfully done with briquettes even without binder.

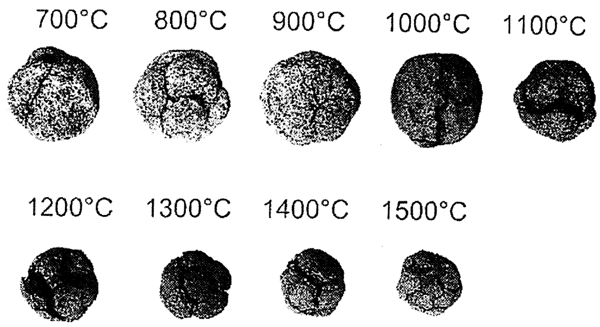

Figure 13. Shrinking of pellets with embedded carbon[72].

Figura 13. Contracción de pellets con carbón embebido[72].

It is well known that the reduction of pellets and briquettes is associated with a volume change. Swelling of agglomerates has two major drawbacks: loss of strength and disintegration, which gives rise to operational problems in reduction furnaces. On the other hand, shrinkage of agglomerates may be profitable for reduction processes because it may increase the strength of pellets and briquettes during the reduction.

Beside the behavior of briquettes pellets with embedded carbon were studied. In these campaign only shrinking was observed[72-74].

To discuss these results in detail further reduction tests were carried out with different ores and different carbon containing materials e.g. coals, char and plastics, see figure 14. Interesting is one of these results, that some pellets show some initial swelling but furtheron only shrinking. By addition special mixture of reduction agents the shrinking behavior can be controlled[75 y 76].

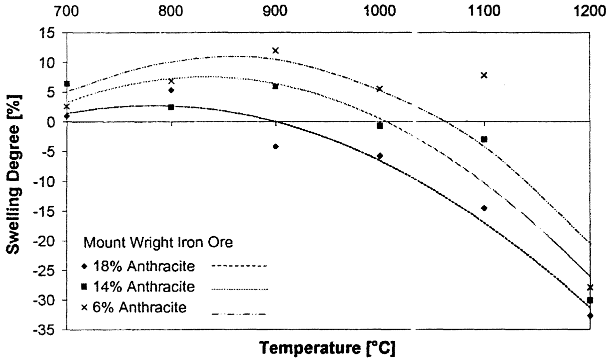

Figure 14. Effect of temperature and anthracite content on the volume change.

Figura 14. Efecto de la temperatura y del contenido en antracita en el cambio de volumen.

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