

# SOME GOOD NEWS: INHIBITION OF THE BOUDOUARD REACTION IN REFRACTORY MATERIALS SUBJECTED TO CO AND H<sub>2</sub> REDUCING ATMOSPHERE

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## ABSTRACT

The catalytic decomposition of carbon monoxide via the reverse Boudouard reaction in the presence of a mixture of CO-H<sub>2</sub> gas produces a solid carbon deposit. This reaction, catalysed by the iron oxides has deleterious effects on refractory materials. The catalytic effects of iron oxides and the structural evolution of carbon during the reverse Boudouard reaction in CO-H<sub>2</sub> atmosphere is investigated at a nano and micro-scale. An inhibition mechanism in a CO + H<sub>2</sub> gas mixture is proposed and validated at lab scale. Solid sulfur compounds inhibit the carbon monoxide dissociation on contact with iron and iron oxides. This result is applied to develop new CO/H<sub>2</sub> resistant refractories.

## INTRODUCTION

The mechanism of carbon monoxide decomposition, called the Boudouard reaction:  $2\text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{C}(\text{s})$  results in the deposition of solid carbon. It causes premature degradation of refractories [1]. This reaction occurs at temperature ranging between 400 to 900°C with a maximum intensity around 600 °C, and is highly favoured by the presence of catalytic particles such as iron and iron oxides. Fe<sub>x</sub>O<sub>y</sub> particles are present in the refractories as impurities in raw materials and by attrition of the mixing devices while blending the refractory formulation.

The CO resistance is usually improved by the selection of raw materials with a low content of iron particles and by raising the refractory sintering temperature. Unfortunately, these solutions are not always very effective for industrial applications where refractories are subjected to CO and H<sub>2</sub> reducing atmospheres (Biomass and Coal Gasification, Steam Methane Reformers, Direct Reduction shafts.....).

The aims of this research are:

- to understand the effect of iron oxides on the carbon formation and to characterise the structural organization of carbon obtained by the reverse Boudouard reaction in CO and H<sub>2</sub> atmosphere
- to find an efficient solution to inhibit the carbon deposit and to limit the degradations of refractories.

## EFFECT OF IRON OXIDES ON THE CARBON FORMATION IN CO, H<sub>2</sub> ATMOSPHERE [2]

Pure iron and iron oxides powders (Fe, FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>), purchased from the Sigma Aldrich and the LKAB companies were used. Microscopic measurements were performed using a thermobalance (Netzch STA 409C/CD) under controlled atmosphere (CO, H<sub>2</sub>, N<sub>2</sub>). The samples, submitted to CO, H<sub>2</sub> atmosphere, were characterised using various techniques: X-ray diffraction, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

## Effect of Fe<sub>2</sub>O<sub>3</sub> grain size on the rate of carbon formation

Fe<sub>2</sub>O<sub>3</sub> with different grain sizes (35 nm, <5 μm, 160-250 μm and 1-2 mm / purity > 99%) was used. Initial specific surfaces of the particles are below 10 m<sup>2</sup>/g, excepted for the 35 nm size (42 m<sup>2</sup>/g). Figure 1-a shows the variation in the sample weight (full lines) based on the thermogravimetric measurements (TGA) as well as the variation in the temperature (black dashed line) as a function of time. At 600°C, the samples were subjected to a gas mixture (composition R: 71% CO, 3% CO<sub>2</sub>, 11% H<sub>2</sub>, 15% N<sub>2</sub>) for 5 hours.

As soon as the gas was injected (at approximately 130 min), a weight loss (approximately 25wt.% for the nanometre grain size) that was associated with the reduction of the Fe<sub>2</sub>O<sub>3</sub> phase in competition with the production of solid carbon was observed. After this reduction, a rapid increase in the weight of the samples was observed (Fig.1-a). This weight gain was primarily due to the production of solid carbon and corresponded to a catalyst/carbon deposition ratio of approximately 1/100 within the asymptotic limit of the Fe<sub>2</sub>O<sub>3</sub> sample. Fig. 1-b shows the normalised weight curve using an asymptotic function of the curves shown in Fig. 1-a. According to the data, the production of carbon appears to be independent of the grain size of the catalyst; the size of the initial grain is not an important parameter for controlling the rate of carbon deposition. However, the smallest grains (35nm) were slightly more reactive and formed more carbon than the largest grains. The largest grains exhibited the slowest formation and produced less carbon.

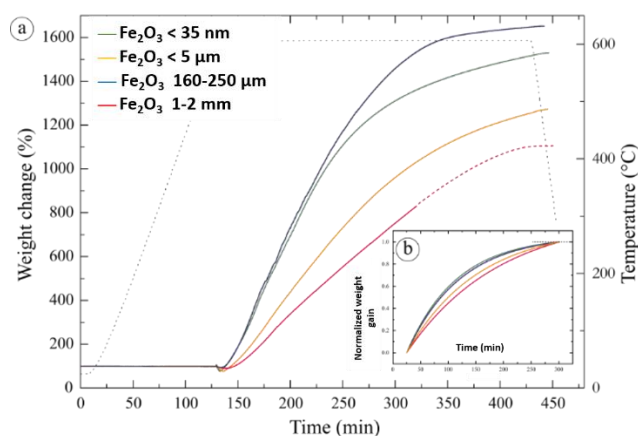


Fig.1: a- Mass variation of Fe<sub>2</sub>O<sub>3</sub> samples versus time depending to the temperature (in black dotted line)  
b- Weight normalised curve

## Effect of the iron valence on the carbon deposition rate

Pure iron and iron oxides (FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) powders were submitted for 5 hours at 600°C under reducing atmosphere (composition R 70% CO, 10% H<sub>2</sub>, 3% CO<sub>2</sub> and 17% N<sub>2</sub>).

The gas flow was 4.2 l/h. Results are reported in Fig. 2-a. As soon as the gas was injected (at ≈130 min), a weight loss (≈25% for Fe<sub>2</sub>O<sub>3</sub>; Fig. 2-b) that was associated with the chemical reduction of the Fe<sub>x</sub>O<sub>y</sub> phase occurs. After this reduction, a rapid increase in the weight of all of the samples was observed, except for the FeO sample, which requires a longer reaction time (≈ 50 min). The reaction produces a large amount of solid carbon (Fig. 2c).

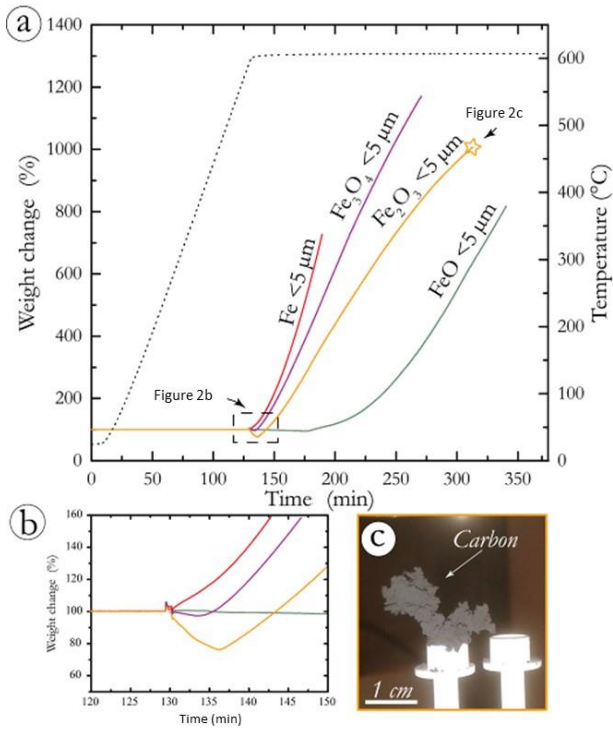


Fig.2: a- Mass variation of the sample as a function of time and temperature (in dotted line). b- Enlargement of the Fig.2 a. c- Carbon deposition in the crucible for the Fe<sub>2</sub>O<sub>3</sub> samples.

The Fe<sub>x</sub>O<sub>y</sub> particles are reduced to metallic iron by the hydrogen. This phenomenon has been described in the literature [3],[4]. In a mixture consisting of CO+H<sub>2</sub> gas, there are many competing reactions including chemical reduction of iron oxides, carbon deposit via the reverse Boudouard reaction and water and carbon formation via the reverse water-gas reactions. It is impossible to distinguish these different reactions in thermogravimetric measurements.

Complementary measurements: XRD and SEM observations (Fig.3) show the quasi complete transformation of a few milligrams of Fe<sub>x</sub>O<sub>y</sub> in pure cementite phase (Fe<sub>3</sub>C). The sp<sup>2</sup> type carbon is formed and is favoured by the catalyst particles. The catalyst grains are highly fragmented to nanometre-sized grains independently of the initial grain size, due to hydrogen effect and the chemical reduction. During the experiment, the Fe<sub>x</sub>O<sub>y</sub> particles were substantially reduced in size.

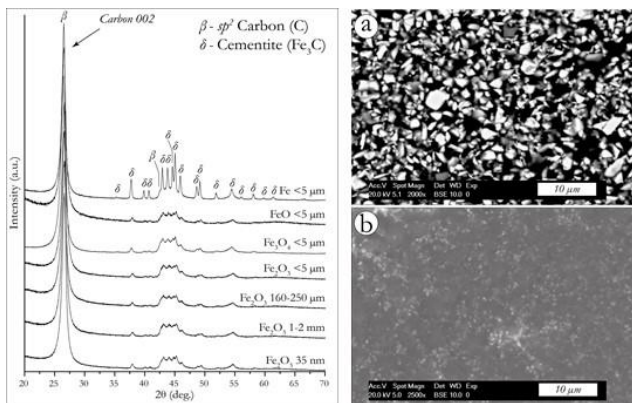


Fig. 3: XRD diffractograms of the "FexOy" samples and backscattered images (a- initial sample Fe<sub>2</sub>O<sub>3</sub> <math>\le 5 \mu\text{m}</math>. b- after CO-H<sub>2</sub> reaction, the size of particles is reduced).

## STRUCTURAL EVOLUTION OF THE CARBON

Raman spectroscopy is an ideal technique to characterise in situ sp<sup>2</sup> carbon materials. It is the most sensitive to explore the full range of the structural states from perfectly crystalline to amorphous [5].

The typical Raman spectrum of "sp<sup>2</sup> carbon" is reported in Fig. 4 and shows three prominent features. The so-called G band located at approximately 1580 cm<sup>-1</sup> and corresponds to the in-plane bond stretching of carbon atoms (E<sub>2g</sub> symmetry). When defects are present, the crystal symmetry breaks down and additional bands appear at specific frequencies depending on the excitation energy used. These bands are called the defect bands: D (≈1250-1400 cm<sup>-1</sup>) and D' (≈1600-1630 cm<sup>-1</sup>). At relatively low defect density, the intensity ratio of the defect-induced D band and the symmetry-allowed G band increases with disorder.

Pure iron and iron oxides powders were submitted for 30 minutes at 600°C under reducing atmosphere: 100% CO and CO+H<sub>2</sub> mixture (industrial gas).

Fig. 4 summarizes the results obtained using Raman spectroscopy and TEM. Raman spectra of the carbon formed in the two types of gas are totally different. G band is observed in the carbon formed under 100% CO and D and G bands are observed when the gas is a mixture of CO and H<sub>2</sub>.

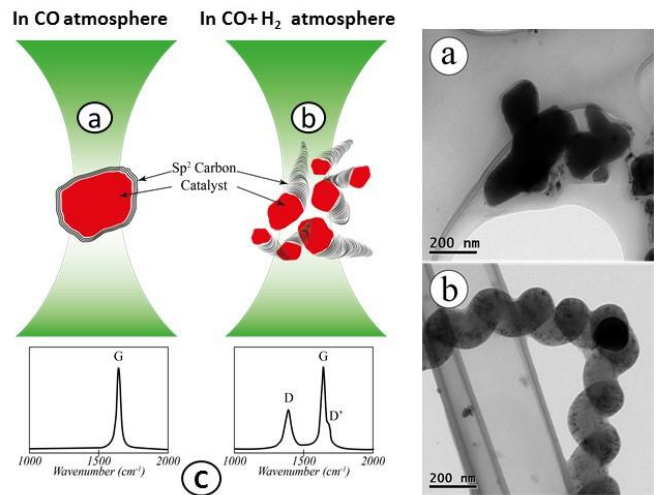


Fig. 4: Schematic representation of the interaction of the Raman excitation laser and the carbon particles in shell around catalyst particles in 100% CO and in nano-fibers in CO + H<sub>2</sub> atmosphere. TEM micrographs of nano-carbon shells and filaments formed à 600°C in a- 100% CO and b- 70.0% CO, 3.0% CO<sub>2</sub>, 10.0% H<sub>2</sub> and 17.0% N<sub>2</sub> from Fe<sub>2</sub>O<sub>3</sub> nanometer size catalyst.

In CO atmosphere, well organized sp<sup>2</sup> carbon is formed around the catalyst particles and the defect-induced D bands are not observed. Only chemical reduction of the catalyst particle occurs without significant size reduction. Therefore, poly-aromatic layers are formed around the catalyst particles in the form of encapsulating shells. These layers are sufficiently large with regards to the laser diameter which explains the no activation of the defect-induced D band in the corresponding Raman spectrum [6]. In CO + H<sub>2</sub> atmosphere, the corresponding Raman spectrum exhibits the defect induced D band suggesting disordered carbon. Catalyst particles are chemically reduced and highly fragmented. Therefore, small-sized carbon nanofibers are formed exhibiting a large amount of poly-aromatic boundaries. This eventually leads to the activation of the defect induced D band without the local structural order being necessarily disturbed [6].

## EFFECT OF SULPHUR COMPOUNDS ON THE INHIBITION OF THE CARBON FORMATION

This part presents an efficient method to inhibit the reverse Boudouard reaction catalysed by the  $Fe_xO_y$  oxides: a low quantity of Sulphur additions prevent the formation of carbon [7].  $Fe_2O_3$  powders were mixed with pure sulphur using different compositions (1, 5, 10 and 30 wt.% of S incorporated in S-  $Fe_2O_3$  mixtures). The samples were heated to  $600^\circ C$  under neutral atmosphere (100 ml/min of Argon), then exposed at  $600^\circ C$  to a CO- $H_2$  reducing gas (30 ml/min of composition R + 70 ml/min of 100% Argon). The results are presented in Fig. 5. Pure  $Fe_2O_3$  shows very important carbon deposits. No weight increases are observed for the samples containing S. During the heating under neutral atmosphere (grey part in Fig. 5), weight loss is directly linked to the vaporisation of the sulphur at approximately  $440^\circ C$ . As soon as the reducing gas was injected (at approximately 58 min, Fig. 5), a weight loss (approximately 25%) is observed, associated with the chemical reduction of the  $Fe_2O_3$  phase by  $H_2$ . After this reduction, an increase in the weight of samples containing S is observed which is stabilized after 300 minutes. This weight variation is linked to the formation of a FeS phase, confirmed by XRD diffraction. At the end of the experiments, we observe that the S additives prevent the carbon formation.

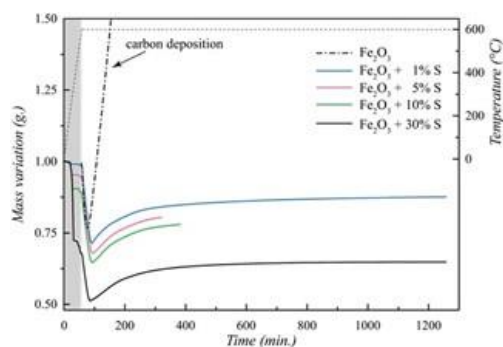


Fig. 5: Mass variation of the samples ( $Fe_2O_3$ + 0-1-5-10-30 wt. %S as a function of time at  $600^\circ C$ )

In a second step, different mixtures containing  $MgSO_4$ ,  $BaSO_4$  and  $CaSO_4$  sulphates were tested in the same experimental conditions. Figure 6 shows the TGA mass variation as a function of time. Pure  $Fe_2O_3$  show important carbon deposits. No weight increases are observed for samples containing sulphates.

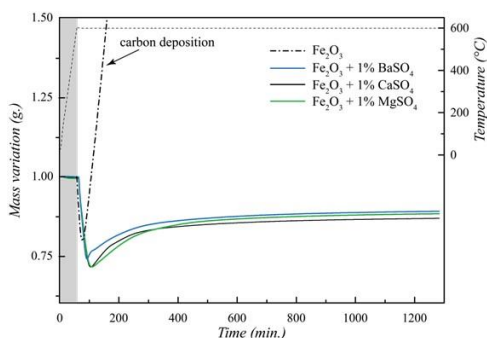


Fig.6: Mass variation of the samples ( $Fe_2O_3$  + 1wt.%  $BaSO_4$ , 1wt.%  $BaSO_4$ , 1wt.%  $MgSO_4$ ) as a function of time, at  $600^\circ C$

## DISCUSSION ABOUT THE MECHANISMS OF CARBON FORMATION AND CARBON INHIBITION BY SULPHUR

The carbon formation by the reverse Boudouard reaction, catalysed by  $Fe_xO_y$ , is a well know process using 100% CO atmosphere.

The iron oxides were essentially converted to iron carbide (cementite). The catalytic deposit of carbon originates from a dissolution-precipitation mechanism. The carbon has a high structural organization and forms polyaromatic shells around big catalytic oxide particles.

When hydrogen is present, the reaction becomes more efficient.  $H_2$  favours the nucleation and growth of carbon filaments on the iron-carbide particles. Figure 7 reports the different steps of the formation of carbon nanofibers by the reverse Boudouard reaction in CO- $H_2$  atmosphere:

- Step 1: Fragmentation of iron oxides to nanometer-sized grains and reduction by  $H_2$  with formation of suboxides of iron ( $Fe_2O_3 \rightarrow FeO \rightarrow Fe$ )
- Step 2: Formation of  $Fe_3C$  nanoparticles
- Step 3: grow of polyaromatic carbon nanofibers

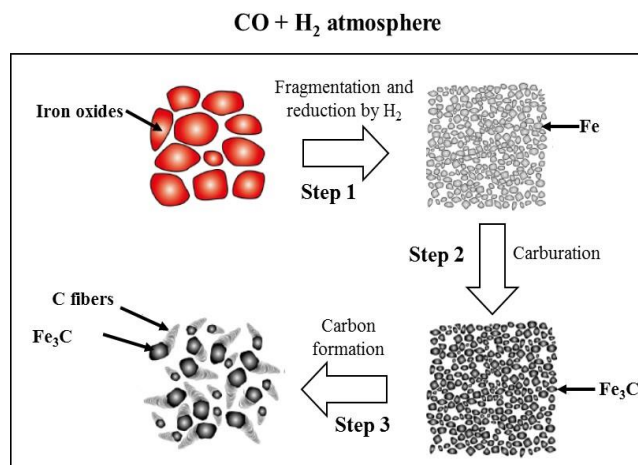


Fig. 7: Mechanism of carbon nanofibers formation by the reverse Boudouard reaction in CO- $H_2$  atmosphere

The mechanism of the carbon formation is inhibited by sulphur or sulphates additions. This result is confirmed by 20 hours experiments in lab. On the surface of the iron oxide particles, FeS or  $FeS_2$  iron sulphides are formed (Fig. 8). The formation of these sulphides can be partial or total depending on the size of the iron oxide particles, the heating time and the reaction time.

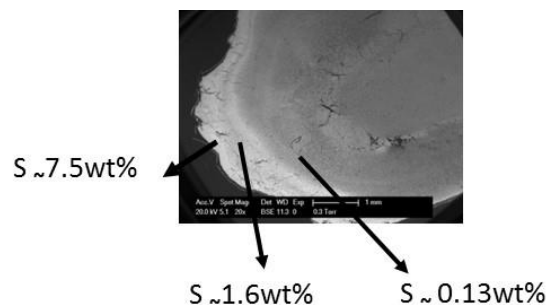


Fig.8: SEM micrograph of iron sulphides at the surface of catalytic iron particles.

Sulfur stabilizes iron carbides so that it can be heated above 600°C without decomposition.

Sulfur does not prevent the reduction of Fe<sub>2</sub>O<sub>3</sub> by H<sub>2</sub> and the fragmentation of the Fe<sub>2</sub>O<sub>3</sub> grains. Nevertheless, it prevents the formation of sp<sup>2</sup> carbon. Sulfur diffuses into the crystallite structure or through the grain boundaries. Moreover, it is not necessary to transform all the iron into iron sulphides to inhibit the reverse Boudouard reaction. Figure 9 reports the mechanism of carbon inhibition in CO-H<sub>2</sub> atmosphere.

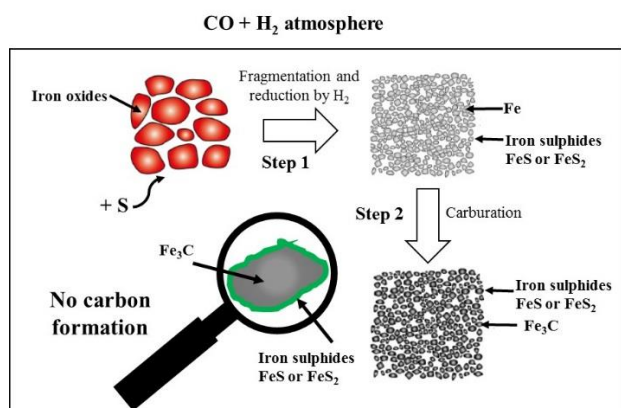


Fig. 9 Inhibition of carbon formation by S in CO-H<sub>2</sub> atmosphere.

#### APPLICATION TO CO/H<sub>2</sub> RESISTANT REFRACTORIES

The benefit effect of S to inhibit the formation of carbon was applied to develop CO/H<sub>2</sub> resistant refractories. Lab experiments were made using a commercial castable. The chemical composition (wt%) of the castable is:

Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>
81	16	2,5	0,6

To promote the formation of carbon and to increase the degradation of refractories, 5 wt.% Fe<sub>2</sub>O<sub>3</sub> nano particles were mixed. Three different formula were prepared and a low quantity of sulphur was incorporated in two samples:

- C1: castable + 5 wt% Fe<sub>2</sub>O<sub>3</sub>
- C2: castable + 5 wt% Fe<sub>2</sub>O<sub>3</sub> and 0,5 wt % solid sulphur
- C3: castable + 5 wt.% Fe<sub>2</sub>O<sub>3</sub> and 3,3 wt.% BaSO<sub>4</sub>

After curing, the three castables were pre-fired in air at 900°C, during 8 hours. Then, they were submitted, for 5 hours, at 600°C under CO+H<sub>2</sub> reducing atmosphere (composition R). Reference powders of pure iron oxide were also tested under the same experimental conditions.

The castable C1 (with 5% wt. Fe<sub>2</sub>O<sub>3</sub>) was destroyed by a “bursting reaction”. A significant carbon deposit in the cementitious matrix was observed and analysed by Raman spectroscopy. The castables C2 and C3 containing S and BaSO<sub>4</sub> additives did not exhibit significant carbon deposit and were not damaged by the reverse Boudouard reaction (Fig.10). These results were confirmed by thermogravimetric analyses (TGA), under reducing atmosphere: composition R: 71% CO, 3% CO<sub>2</sub>, 11% H<sub>2</sub>, 15% N<sub>2</sub>.

However, the effect of S additives to inhibit the formation of carbon has limits: the sulfur additives become ineffective beyond 900 ° C. In some industrial applications, the refractories are subjected to cyclic conditions: oxidizing and reducing. Under these conditions, the stability of FeS and FeS<sub>2</sub> is not guaranteed

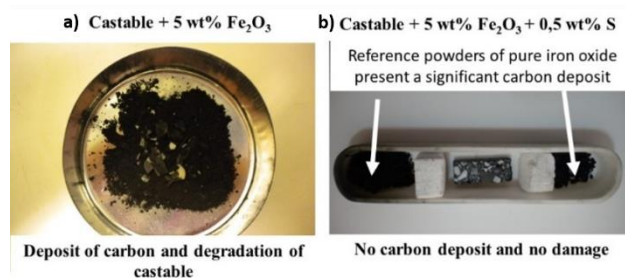


Fig. 10 a- carbon deposit and destruction of C1. b- Effect of sulphur on C2 and C3 castables after exposure to reducing gas.

#### CONCLUSION

The carbon deposit in refractories is catalysed by iron and iron oxides. This reaction is highly favoured by the presence of H<sub>2</sub>. Lab experimentations show that sulphur additives inhibit the CO dissociation and the formation of carbon. This result is applied to CO+H<sub>2</sub> resistant refractories.

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