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## **Role of Wustite in Sand Ageing**

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### ***Introduction***

The sand in fluidized bed is traditionally treated as an inert material. In discussions on the influence of the bed materials, the sand is often completely forgotten. Usually the sand comes from the local sources and can consist of wide range of elements. For example, practically all minerals and soils contain iron, which ranks second in abundance among metals and fourth among all elements (Holtclaw, 1991).

Iron oxides can appear in fuel and in char as well as in sand. Iron among bed material is a well-studied subject; several studies on it have been published, eg. Johnsson and Dam-Johansen, 1991, Zevenhoven and Hupa, 1998, Miettinen et al., 1991, Olanders and Strömberg, 1995, Aho et al., 1991, and Hayhurst and Lawrence, 1997. In tests where carbon monoxide was combusted in different natural sand beds, the most active sand contained more iron than the others did (Olanders and Strömberg, 1995). Aho et al. (1991, 1990) studied catalytic effects of metals on peat combustion in an entrained flow reactor and with

thermogravimetric experiments. They indicated that iron clearly decreases the burnout times and reaction peak temperatures of peat.

Carbon monoxide is the most important gaseous intermediate product when burning carbon-containing fuels in the fluidized bed. CO is a strong reducing agent and large concentration differences may occur in the fluidized bed, as formation of reducing zones is obvious. Many natural minerals include iron compounds and impurities of iron. In the blast furnaces iron oxides are reduced with CO. Similar conditions may appear in fluidized beds. Also, iron oxides are known to act as a catalyst in the oxidation of CO.

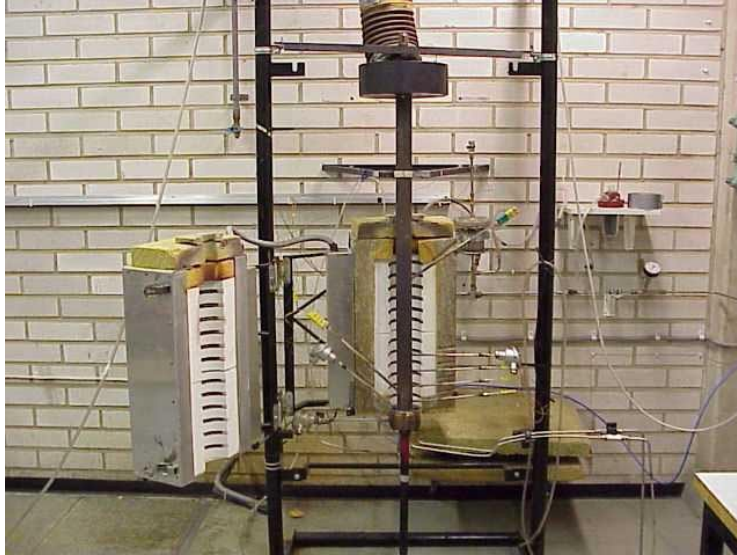
Reduction of iron oxides has been intensively investigated and reported by many researchers during last 40 years. The main target has been to improve the properties of iron and steel in base metal production. Still, the conditions are very similar to those in fluidized bed combustion. In this study the knowledge from making iron is used to improve the understanding of the fluidized bed combustion.

## ***2. Experimental***

The laboratory scale fluidized bed reactor is a fire-resistant steel pipe with an inner diameter of 42 mm. The reactor is surrounded with an electric heater. The temperatures in the bed are measured with thermocouples. Five of these are radially assembled through the reactor wall 50 mm apart, the lowest one being at the surface of the distributor plate. Earlier studies have proved that the effect of the fire-resistant steel pipe on the reactions is negligible.

Temperature and gas concentrations were measured continuously during the test runs. Gas samples were taken from different levels inside the bed. They were first sucked through an air-cooled sample probe, then cooled in a refrigerator and finally concentrations of CO, CO<sub>2</sub> and O<sub>2</sub> were analysed with separate analysers. Inlet gas flows were totally mixed before they reached the bed and the flow rates of gases were controlled by digital mass flow controllers. The bed height was 18 - 22 cm in the unfluidized state and the particle size was 250-500 µm. Carbon monoxide was used as a fuel in combustion tests and as a reductive gas in tests under reductive conditions. Air and nitrogen were used as fluidizing gases. To imitate the conditions inside a bubbling fluidized bed in emulsion phase, all experiments were conducted without

present bubbles. The fluidized conditions varied due to different bed materials from partial to minimum fluidization.



**Figure 1.** Test rig used in experiments.

### ***3. Effect of Sand Composition***

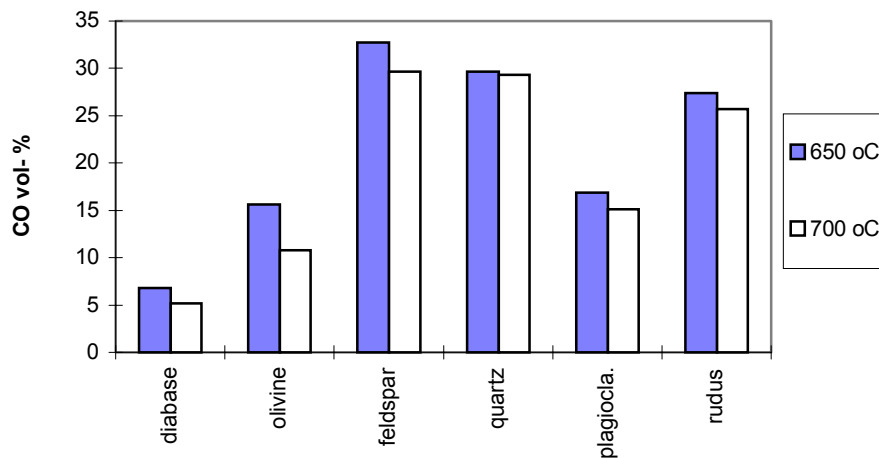
The sands most used in experiments were so called Lohja Rudus sand and diabase sand. Lohja Rudus sand (provided by Lohja Rudus Oy) is typical Finnish quartz sand consisting mainly of three minerals: quartz, plagioclase and feldspar. Diabase is composed mostly of plagioclase and olivine. It also contains small amounts of augite, magnetite, sausalite and minor quantities of other minerals. Also pure quartz sand, pure feldspar and pure plagioclase sands were used in experiments. Hematite ore (particle size 250 - 500  $\mu\text{m}$ ) was used to increase the iron content of the sand in some tests. Limestone was used in tests under nonoxidative conditions. The elements of the minerals used are shown in Table 1.

**Table 1.** Elements of examined minerals in weight-% determined with SEM/EDS.

|    | diabase | feldspar | limestone | olivine | plagioclase | quartz | hematite | rudus |
|----|---------|----------|-----------|---------|-------------|--------|----------|-------|
| Na | 6       | 9        |           | 2       | 9           | 1      |          | 3     |
| Mg | 6       | 1        | 2         | 23      | 3           |        |          | 1     |
| Al | 19      | 21       |           | 5       | 24          | 2      | <1       | 14    |
| Si | 39      | 52       | 2         | 21      | 36          | 95     | 6        | 67    |
| P  | <1      |          |           | <1      | 1           |        |          |       |
| S  | <1      |          |           | <1      |             | 1      |          |       |
| K  | 2       | 16       |           | 1       | 2           |        |          | 7     |
| Ca | 10      | <1       | 96        | 2       | 13          | <1     | <1       | 3     |
| Ti | 1       |          |           | 5       | 3           |        |          | 1     |
| Fe | 16      |          |           | 40      | 8           |        | 93       | 5     |

### Tests under substoichiometric conditions with different sands

Oxidation of carbon monoxide was studied with different natural sands in a laboratory scale fluidized bed in substoichiometric conditions. The experiment revealed that the composition of the sand has an effect on conversion of CO. Diabase, olivine and plagioclase sands were found to be the most active of the sands studied. They proved to be effective even in lower temperatures (the reactor wall temperature 650°C). Figure 2 shows the measured CO concentration 100 s from the beginning of the test 20 cm above the distributor plate.

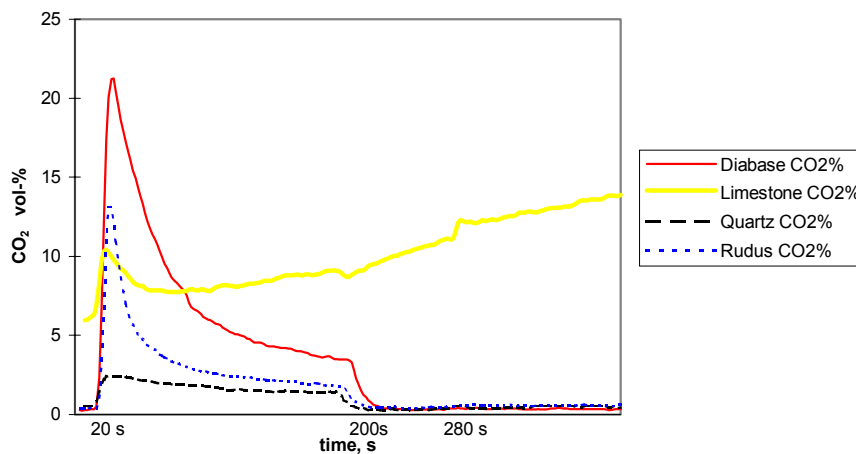


**Figure 2.** Carbon monoxide concentration (vol-%) in the bed (200 mm above the distributor) with minerals 100 s from the beginning of the test. Bed height was 20 cm in unfluidized state, the particle size was 250-500  $\mu\text{m}$  and the relative air/ fuel ratio was 0.7. Fluidizing velocity was 6.2 cm/s.

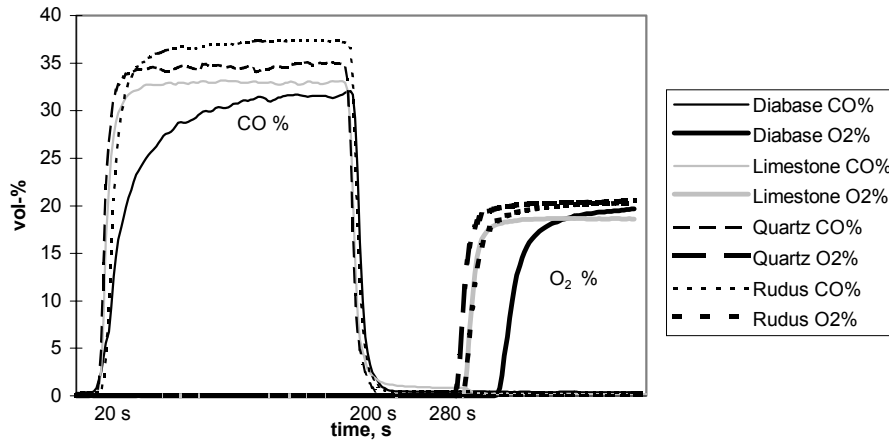
## Tests under nonoxidative conditions

The tests under nonoxidative conditions were conducted with diabase, rudos and quartz sands and limestone. Pure rudos and rudos with 1, 5 and 10 weight-% of hematite were used. The reactor wall temperature was adjusted to 650 or 700°C and bed height was 20-21 cm with all sand mixtures. Nitrogen was used as fluidizing gas. CO flow was introduced to the bed at 20 seconds and stopped at 200 seconds. At 280 s nitrogen was replaced with air.

In nonoxidative conditions the measured concentration of CO<sub>2</sub> in the bed (20 cm above the distributor) increased quickly with diabase, rudos and limestone, when CO reached the bed. In quartz bed the increase in concentration of CO<sub>2</sub> was quite small. CO<sub>2</sub> concentration started to decrease after a few seconds with most bed materials, but with limestone the concentration of CO<sub>2</sub> remained high, probably due to calcination. In quartz bed the CO<sub>2</sub> concentration was about 1-2 %. CO<sub>2</sub> peaks are shown in Figure 3.



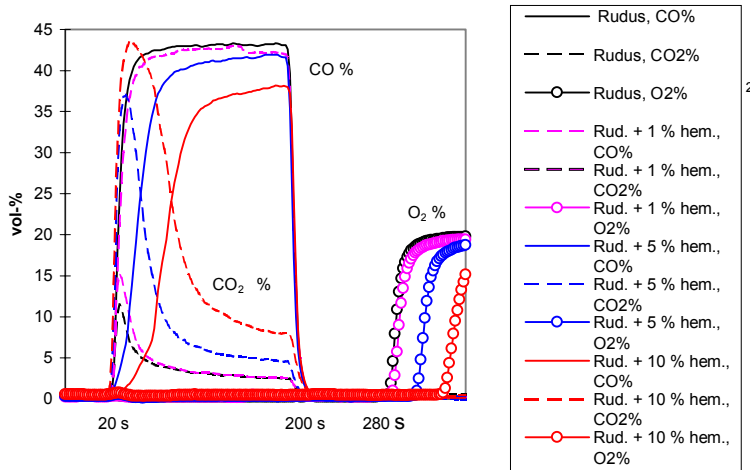
**Figure 3.** Measured CO<sub>2</sub> concentrations 20 cm above the distributor in nonoxidative conditions with diabase, limestone, quartz and rudus sands as bed material. Wall temperature was adjusted to 650°C, bed height was 22 cm and fluidizing velocity was 7.0 cm/s with rudus, 8.6 cm/s with limestone, 10.4 cm/s with diabase and 12.1 cm/s with quartz. CO flow was started at 20 s and stopped at 200 s. The fluidizing gas was first nitrogen and at 280 s it was replaced with air.



**Figure 4.** Measured CO and O<sub>2</sub> concentrations at 20 cm above the distributor in nonoxidative conditions with diabase, limestone, quartz and rudus sands as bed material.

CO flow was stopped at 200 s. The fluidizing gas was replaced with air at 280 s. Figure 4 shows that oxygen concentration in the gas sample increases later in the diabase bed. The temperature increased rapidly when air was introduced to the bed. The increase in the temperature was biggest at thermocouple 4. With diabase the temperature rose 22°C, with rudus 17°C, with quartz 13°C and with limestone 14°C. The temperature peak is apparently caused partly by the oxidation of the FeO. As the rapid rise of the temperature, only weaker, can be observed also with sands not containing iron, there must be other exothermic reactions taking place in the beds examined.

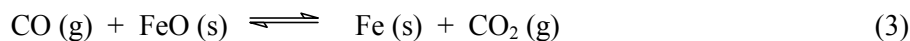
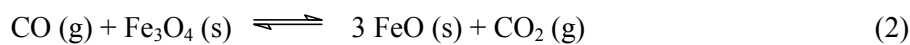
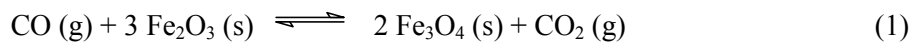
Similar tests in nonoxidative conditions were conducted using hematite mixed with rudus sand. The increase in CO<sub>2</sub> concentration was remarkably bigger with 5 and 10 weight-% hematite mixed with rudus than with pure rudus and rudus with 1 % of hematite, after CO had been introduced to the bed. CO<sub>2</sub> concentrations were 44 vol-% with 10 % hematite, 38 % with 5 % hematite, 16 % with 1 % hematite and 12 % with pure rudus. Gas sample concentrations (20 cm above the distributor) are shown in Figure 5. Nitrogen was used as the fluidizing gas in the beginning of the test. Figure 5 shows a delay in the increase of the oxygen concentration with higher hematite concentrations after oxygen is introduced to the bed, which indicates that the Fe<sub>2</sub>O<sub>3</sub> will reduce to FeO.



**Figure 5.** Gas sample concentrations in nonoxidative conditions at 20 cm above the distributor using pure rudos and rudos mixed with 1, 5 and 10 % hematite in the bed. CO flow was turned on at 20 s and turned off at 200 s. The fluidizing gas was nitrogen in the beginning of the test and it was replaced with air at 280 s. The fluidizing velocity was 9.1 cm/s. The wall temperature was adjusted to 700°C and the bed height was 21 cm.

When the fluidizing gas was changed from nitrogen to air, the temperature started to increase. Small differences were observed in the increases of the temperature. As the temperature rose 26°C with pure rudos, the change in the temperature was 32°C with 1% hematite, 38°C with 5% hematite and 39°C with 10% hematite mixed with rudos, respectively.

CO reacting with the oxygen adsorbed from the surface of the sand would probably explain the CO<sub>2</sub> concentrations. CO also seems to reduce iron oxides of the sand. Similar reduction reactions take place in the blast furnaces where iron ores are reduced with CO.



The colour change in the sand, in diabase in particular, was clearly visible. The new, unused diabase is grey. During the experiments in reductive conditions and cooling in non-oxidative atmosphere, it turned darker grey. When air was introduced to the reactor, the sand in the bed turned reddish. The three fractions were analysed by XPS. Analyses indicate that reactions (1) and (2) took place in the tests under reductive conditions: bond energies indicate that iron is partly in the form FeO, which is black in colour. The differences between the bond energies leave no place to err. The bond energies of other elements in the samples do not vary. The bond energies of iron indicate that iron is in the form Fe<sub>2</sub>O<sub>3</sub> in the fresh sand and the sand that

has been in the combustion of CO and partly in the form FeO after being in reductive conditions.

Diabase contains magnetite ( $\text{Fe}_3\text{O}_4$ ), which is black. XPS analyses did not show any  $\text{Fe}_3\text{O}_4$  to be present. That indicates that few atom layers on the surface of the sand may be oxidated to  $\text{Fe}_2\text{O}_3$ , which is reddish, but the layer may be too thin to affect the colour of the fresh sand.

Observations of changes in the bed material during combustion have been made. Miettinen et al. (1991) indicated that decomposition of  $\text{N}_2\text{O}$  with magnetite is not a catalytic process, but magnetite seems to oxidate to hematite. The colour of magnetite changed from black to brownish red. Olanders and Strömberg (1995) found similar colour change in olivine sand, which contains iron oxides. Also Vural (1997) observed colour changes in different bed materials. He concluded that fluidizing particles behave distinctively during devolatilisation of coal particles, or that the interaction between the volatile matter and bed solids is different for each kind of particle. The article did not mention if iron oxides were present in the beds examined.

### **Oxidation of CO before and after strongly reductive conditions**

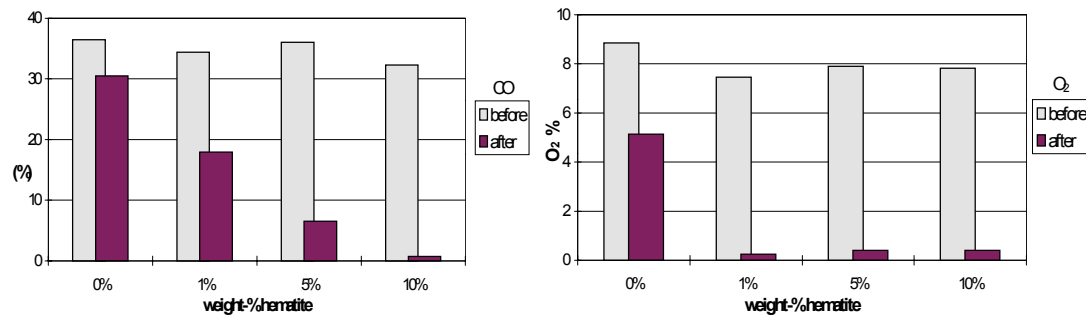
The oxidation of carbon monoxide was investigated before and after strongly reductive conditions. The conditions created were extreme to obtain a more precise picture of the influence of iron oxides in reductive and oxidative conditions. In the first set of tests carbon monoxide was oxidated by air: the bed was fluidized by air and CO flow was introduced to the bed for 100 s and then stopped. The temperature was stabilised between the tests. The oxidation test was repeated four times with all sands. After the oxidation tests the bed was fluidized by nitrogen gas in nonoxidative conditions, CO flow was introduced to the bed at 20 s and stopped at 200 s. At 280 s nitrogen was replaced with air. Again, four repetitive tests were conducted. The oxidation of CO was re-examined after reductive conditions. After 180 s of strongly reducing conditions, the oxidation rates of carbon monoxide had improved remarkably even in the rudus without added hematite. The more hematite the sand contained the more the oxidation rates improved.

The oxides of iron obviously take part in the reactions and the reductive conditions emphasize the effect of iron. The reduced oxides of iron seem to be more active in the oxidation of CO than hematite ( $\text{Fe}_2\text{O}_3$ ). The effectiveness of an iron catalyst in the gasification of carbon has been found to depend on the oxidation state of the iron. According to Illán-Gómez et al.



(1995), the oxidation state of the metal determines its performance. The catalyst is effective when it is in reduced state. The catalytic activity of metallic iron decreases sharply when it is oxidated. The reduced iron compound accepts oxygen deposits on its surface and is transformed to oxidated forms. The oxygen is transferred from the catalyst to the reactive compound and iron species recovers its reduced state. In fluidized beds iron takes part in the catalytic redox cycle. Ohtsuka et al. (1986) showed that even magnetite,  $\text{Fe}_3\text{O}_4$ , promotes some of the gasification of coal; despite that earlier only metallic iron had been claimed to be catalytically active. It can be assumed that iron oxides with lower oxidation states are better reducing agents in the oxidation of carbon monoxide (Illán-Gómez et al., 1995, Hüttinger, 1983).

Figures 6 and 7 summarize the volume percentages of carbon monoxide and oxygen in the gas samples from the beds 100 seconds from the start of the test before and after strongly reductive conditions.

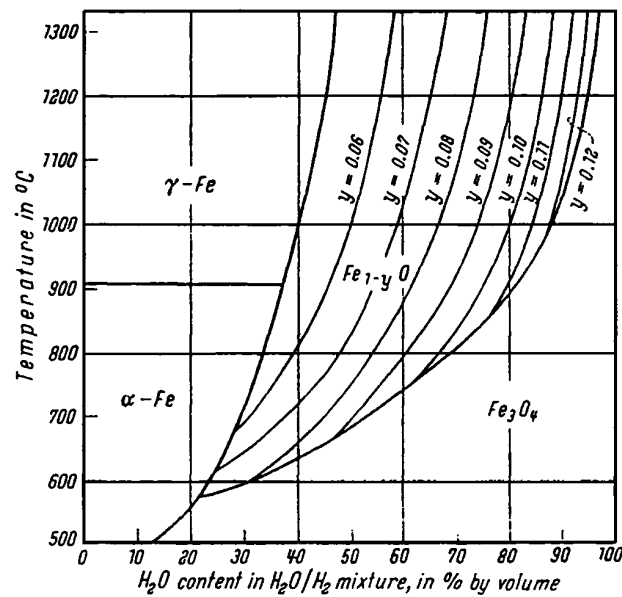


**Figures 6 and 7.** Carbon monoxide and oxygen concentrations (vol-%) in the bed (20 cm above the distributor) 100 seconds after the test was started. The fluidized bed sand was rudus containing 0, 1, 5 and 10% of hematite. Bed height was 21 cm in unfluidized state, the particle size was 250-500  $\mu\text{m}$  and relative air/fuel ratio was 1. Fluidizing velocity was 7.2 cm/s (Roppo, 1998).

Figures 6 and 7 point that the reductive conditions as well as the hematite content of the bed have an effect on the conversion of CO. The effects of reductive conditions can also be seen with pure rudus in the bed. Rudus contains approximately 5% iron compounds, which indicates that also with rudus in the bed the oxidation and the reduction of iron may cause the phenomenon. In the beds containing more iron the phenomenon is more noticeable.

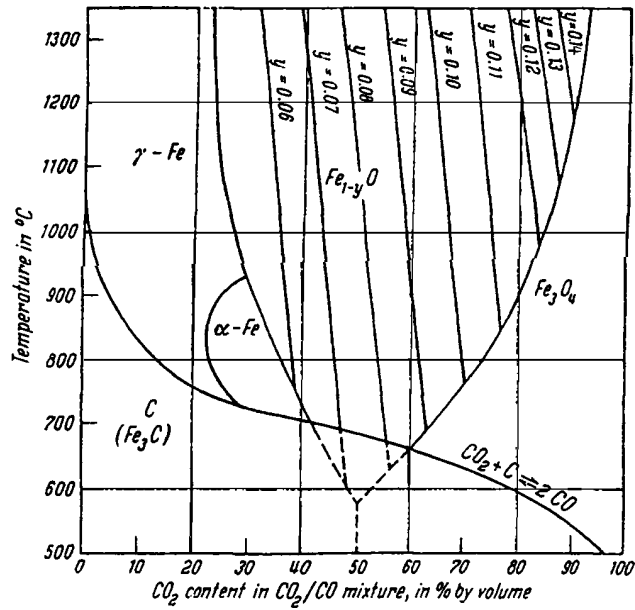
#### 4. Sand ageing

There exists an intermediate state of iron oxide, which may have an important role in sand ageing. It is called wustite ( $\text{Fe}_{1-y}\text{O}$ ). This iron oxide has ability to change its state of oxidation between  $y=0.05$  and  $y=0.15$  depending on the surrounding conditions. In Figure 8 the equilibrium between iron, wustite and magnetite is shown when reducing agent is hydrogen.



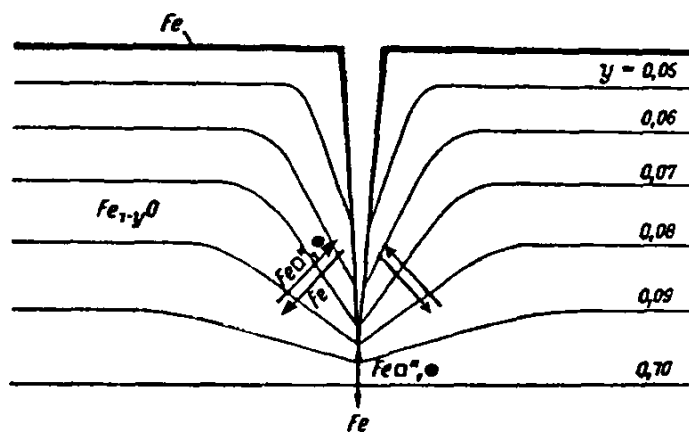
**Figure 8.** Equilibrium between iron, wustite, magnetite and hydrogen and water-vapour mixture (von Bogdandy et al. 1971).

With carbon monoxide the equilibrium is different. This is shown in Figure 9. Both figures show that any value of  $y$  is possible. On the surface of the sand particle there can be pure metallic iron while inside the particle all states of oxidation are possible. This phenomenon causes formation of fine pores during the reduction. These fine pores increase the active surface area of the sand particle. The mechanism is shown in Figure 10.



**Figure 9.** Equilibrium between iron, wustite, magnetite and carbon monoxide, carbon dioxide and carbon (von Bogdandy et al. 1971).

The specific surface area of fresh sand and aged sand were measured. The results showed that the surface was reduced during sand ageing. That was due to a mistake in sand storing. The metallic iron on the surface of the sand particle may be oxidated even in the room temperature if there is oxygen present. The iron was covered with a thin layer of iron oxide blocking the thin pores. When the sand was introduced again into reducing conditions the thin layer quickly reduced re-liberating the original area.



**Figure 10.** Formation of fine pores during the reduction of wustite with an excess of cation vacancies (Kohl et al. 1963).

## **5. Conclusions**

Sand ageing has been a mystery for some time. Reactivity of fresh sand is usually low, but it increases in reducing conditions in a function of iron content of the sand. The mechanisms, though, have not been known.

When iron oxides reduce to wustite, the formation of the fine pores starts. These fine pores increase the active surface area of the sand particle and thus increase the reactivity. In the presence of oxygen the pores are covered with iron oxides. Re-introducing the particle to reducing conditions reduces the thin oxide layer; hence the reactivity of the particle improves.

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