

AN APPLICATION OF A HIGH-TEMPERATURE AND HIGH-PRESSURE REACTOR - part II

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Preliminary Note - Prethodno priopćenje

A prototype of a high-temperature and high-pressure reactor generating on oxygen-hydrogen flame used for gravity separation of multiple mineral components is already in its fourth year of development. This equipment, applied in a high temperature range, will be able to treat the waste of some industrial technologies, which are of multiple component nature. [Metalurgija 41 (2002) 3, 139 - 142]. The results of the project received by the february of 2003 are listed in this article.

Key words: *oxygen-hydrogen reactor, high-pressure, high-temperature, power unit, high-pressure chamber, oxygen-hydrogen generator*

Primjena visoko-temperaturnog i visoko-tlačnog reaktora (drugi dio). Već se dvije godine razvija prototip visokotemperaturnog i visokotlačnog reaktora koji koristi plamen kisika i vodika, a primjenjuje se za gravitacijsku separaciju višekomponentnih mineralnih smjesa. Ova oprema, primjenjena u opsegu visokih temperature, omogućit će obradu višekomponentnih otpada nekih industrijskih tehnologija, koje su višestruko složene prirode. [Metalurgija 41 (2002) 3, 139 - 142]. U članku se daju rezultati istraživanja do veljače 2003.

Ključne riječi: *kisik-vodik reaktor, visokotlačni, visokotemperaturni, energetska jedinica, visokotlačna komora, generator kisika i vodika*

INTRODUCTION

The hydrogen reactor makes it possible not only to process the rocks based on the gravity classification principle of the elements which are present in the melt, but also to form new compounds with the water vapours presence and under the conditions of high temperatures and high pressures. These processes require equipment enabling the melting and the test material solidification under high temperatures and pressures as well.

The design of the power unit was suggested as an oxygen-hydrogen flame generator with the combustion temperature of up to 3000 K. The main component of the flame generator is a starting cell from a jet-fighter aeroplane adjusted for separate supplies of a fuel (hydrogen) and an oxidizer (oxygen) through electromagnetic regulation valves (Figure 1.). The reactor is designed for the pressure of 16 MPa, however such values are not attainable due to the insufficient regulation elements.

Note: We were not able to measure the relevant values of temperatures in any series of "sharp" tests. We used the term "sharp" test for tests during which samples were melted. These tests have been preceded by the series of tests aimed to verify the functionality of the individual regulating, controlling and measuring elements. The reliability of the controlling burner, release valve were tested and the output velocities of the media itself were measured.

We tried to measure temperatures in various locations of the reacting zone using a variety of thermometer types in course of the individual tests. The selected concept of the temperature measurement was unsuitable and thermometers have lost gradually their functionality. In future we intend to use either pyrometer or thermovision camera.

THERMODYNAMIC CALCULATIONS OF SOME SYSTEMS

The atmosphere originated after the hydrogen combustion in the high temperature and high pressure facility consists mainly of water vapour. Along with it nitrogen, oxygen and possibly hydrogen may also be present. The gaseous atmosphere of the water vapour under increased tempera-

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Figure 1. Power unit
Slika 1. Energetska jedinica

ture and pressure shall physically and chemically effect some components of rocks. Based on the thermodynamic calculations it is possible to estimate what physical and chemical changes will occur under the increased temperatures and pressures. The objective of the thermodynamic calculations is to determine whether the chemical changes between the rocks (SiO_2 , FeO , Al_2O_3 , CaO , MgO) and water vapour will occur under the given conditions (Figure 2.).

The thermodynamic parameter determining the course of the spontaneous phenomena in the system under the isothermal and isobaric conditions is free energy F , which can be mathematically expressed as follows:

$$F = U - T \cdot S \quad (1)$$

or its change

$$\Delta F = \Delta U - T \cdot \Delta S \quad (2)$$

where:

U - internal energy,
 S - entropy,
 T - absolute temperature.

The course of the spontaneous phenomena under the constant temperature and volume will show the drop in the system free energy, what means that the system is able to do work under the given conditions. Should the chemical reaction accompany this process, then the spontaneous phenomena will proceed in the shown direction, i.e. from the left to right. In case of the isothermal phenomena, the course of the spontaneous phenomena is characterised by the thermodynamic parameter - free enthalpy G , defined mathematically as follows:

$$G = H - T \cdot S \quad (3)$$

or its change:

$$\Delta G = \Delta H - T \cdot \Delta S \quad (4)$$

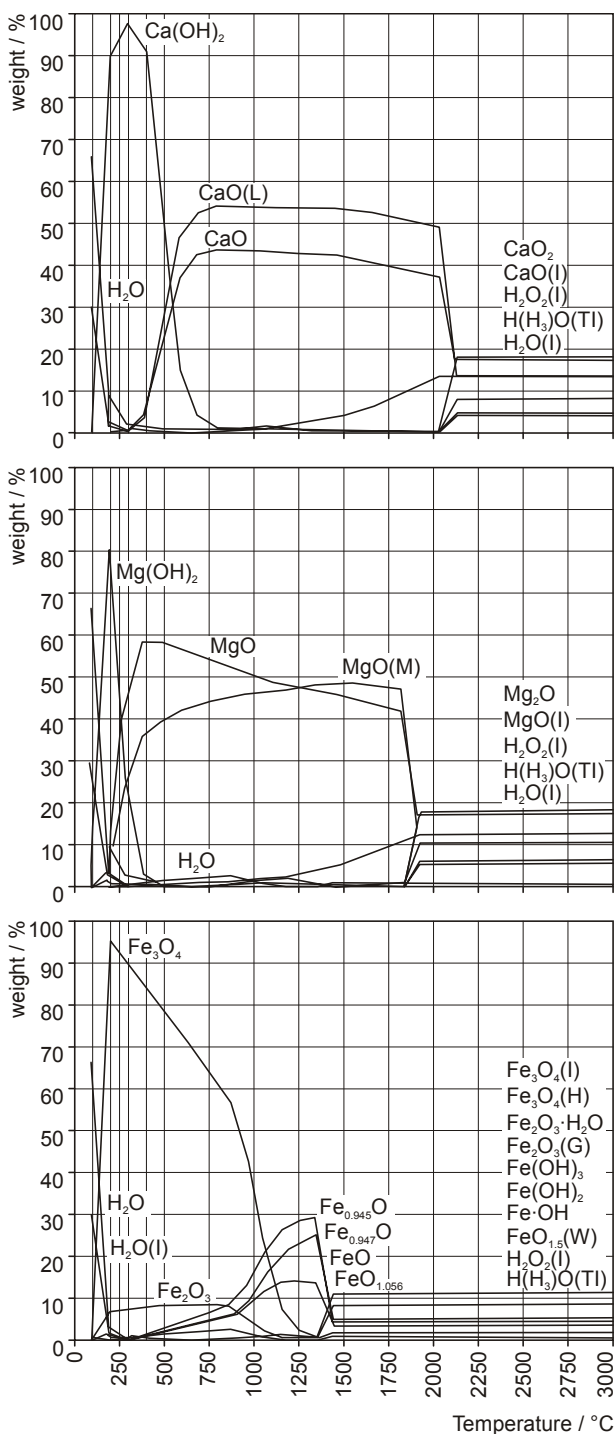


Figure 2. Equilibrium of the: $\text{CaO-H}_2\text{O}$, $\text{MgO-H}_2\text{O}$, $\text{FeO-H}_2\text{O}$ systems

Slika 2. Ravnoteža sustava: $\text{CaO-H}_2\text{O}$, $\text{MgO-H}_2\text{O}$, $\text{FeO-H}_2\text{O}$

where:

H - enthalpy.

The spontaneous course of the reactions is characterised similarly as in the previous case of the isothermal and isobaric phenomena. The numerical value of the equilibrium constant of the chemical reaction shows, along with the thermodynamic parameters of the free energy and free enthalpy, whether the reaction is shifted to the left or to the right. High values of the equilibrium constant confirm unambiguously the spontaneous course of the reaction in the shown direction under the given conditions.



Figure 3. **Melting process**
Slika 3. **Proces taljenja**

The thermodynamic parameters of ΔH , ΔS and ΔG under the standard conditions and the values of the equilibrium constant K of the chemical reactions were calculated. The calculations provide the only information, whether the reaction will be spontaneous or not in the temperature interval 100 through 2600 °C.

RESULTS OF CALCULATIONS

There is no spontaneous reaction in the system $\text{SiO}_2 - \text{H}_2\text{O}$, i.e. the SiO_2 hydration does not occur.

The number of compounds if formed within the temperature interval up to 3000 °C.

$\text{Ca}(\text{OH})_2$ is formed in the temperature interval of 100 to 500 °C in the system $\text{CaO}-\text{H}_2\text{O}$. The above reaction is not possible over the temperature of 600 °C from the point of view of thermodynamics.

$\text{Mg}(\text{OH})_2$ is formed in the temperature interval of 100 to 200 °C in the system $\text{CaO}-\text{H}_2\text{O}$. The above reaction is not possible over the temperature of 300 °C from the point of view of thermodynamics.



Figure 4. **Rock samples after the flame action**
Slika 4. **Uzorci stijene nakon obrade plamenikom**

There is no spontaneous reaction in the system $\text{Al}_2\text{O}_3 - \text{H}_2\text{O}$, i.e. the $\text{Al}(\text{OH})_3$ formation does not occur.

$\text{Fe}(\text{OH})_2$ is formed at the temperature of 100 °C in the system $\text{FeO}-\text{H}_2\text{O}$. The above reaction is not possible over the temperature of 200 °C from the point of view of thermodynamics. However, the oxidation FeO to Fe_2O_3 may occur within the temperature interval of 100 through 600 °C and then $\text{Fe}(\text{OH})_3$ is formed.

There is spontaneous reaction in the system $\text{FeCO}_3 - \text{H}_2\text{O}$ and Fe_3O_4 and gaseous reactants H_2 and CO_2 formation occur in the temperature interval of 100 to 1000 °C.

EXPERIMENTAL

The experiments, including the rock and synthetic samples melting, were performed under the following conditions:

- regulation valve of hydrogen flow - open: 10 to 21 %,
- regulation valve of oxygen flow - open: 10 to 22 %,
- input hydrogen pressure: 2,2 to 3,4 MPa,
- input oxygen pressure: 2,4 to 3,6 MPa,
- maximum pressure in tank (TN): 0,8 MPa,
- time of flame acting on sample: 50 through 300 s,
- time of pressure drop in TN: 50 through 300 s*,
- samples melting temperature: 1470 through 2890 °C**.

*As already mentioned in the introduction, insufficient regulation elements did not allow us to work with the pres-

tures for which the pressure tank is designed. This resulted also in time interval of the pressure drop in the pressure tank after switching off flame. This time interval was too short and did not correspond to our expectations.

**Provided values are taken from the tables and do not represent the results of our measurements.



Figure 5. Molten basalt in carbon container
Slika 5. Rastaljeni bazalt u ugljičnom spremniku

The results of the experiments are rather variable, some of them are highly interesting, and some are unsatisfactory. However, the variety of the results is typical for the begin of such experiments (Figure 4., 5.). The brief review of the individual samples change, resulting from the flame action in the hydrogen reactor, which have been subjected to the microscope and X-ray analysis, is as follows:

- FeO : new phases - Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$,
- Al_2O_3 : Al_2O_3 - corundum,
- CaO : CaCO_3 - traces only
 - reaction with the material - $\text{C}_{12}\text{Al}_{14}\text{O}_{33}$ of crucible used for tests,
- MgO : no changes,
- SiO_2 : SiO_2 - cristobalit (recrystallisation),
- polymetallic ore (siderit, tetraedit,...): after X-ray analysis- siderit, magnetite
 - maghemite, hematite, inclusions of Ag -tetraedit,
- zealot: sample almost evaporated, could not be analysed.

CONCLUSION

Our objective was to try to observe the rocks properties not observed until now. New technologies executed under the conditions of high temperatures and pressures make it possible to process them to purer materials and elements. Obtained knowledge gives an assumption to design new technologies making it possible to treat the low quality materials, some polymetallic ores, as well as ferrous and non-ferrous ore.

Further possibilities are shown for the waste with high silica content processing as well as the waste of the complex materials.

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