

INVESTIGATION OF PROCESSES FOR HYDROGEN OBTAINING BY IRON-STEAM METHOD WITH THE USE OF METALLURGIC WASTE UNDER HEATING BY CONCENTRATED SOLAR ENERGY

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Introduction

The main source of hydrogen obtaining under industrial conditions is water. Many methods of conversion are used for this purpose taking into account also the property of many metals to displace hydrogen from water with simultaneous formation of the taken metals hydro-oxides or oxides. Iron-steam method is one of the most spread being used in the investigation of hydrogen obtaining processes.

The goal of the given work is to investigate the opportunity to carry out cyclic processes of reduction and oxidation of multicomponent iron-containing mass of "Integrated metallurgical Co. "Azovstal" waste by water steam. The investigation has been carried out on automated thermogravimetric installation.

Results and Discussion

The installation and method for generator gas obtaining have been developed for carrying out reducing cycles. The method is based on the reaction of formic acid decomposition in sulphuric one. Kinetic conditions are determined for its obtaining and it has been established that it is necessary to take into account the reaction of CO₂ formation and take care to decrease dioxide concentration for obtaining high-quality reducing gas. It is possible by ensuring the conditions for its interaction with carbon, sufficient time of reaction contact and optimum temperature conditions.

The rate of carbon interaction with its dioxide depends upon temperature and carbon nature and CO decomposition rate- upon the used catalyst, which is iron in our case. In connection with this it is necessary to take appropriate measures during the reduction process to avoid blocking active surface by iron-containing component.

By the attainment of equilibrium in the reaction of carbon gasification the composition of gaseous phase does not depend upon the system initial state. The comparison of experimental and calculated data is presented in the Fig. 1 from which it is obvious that under atmospheric pressure

the interaction between CO₂ and C under 450 °C does not cause CO formation when under 1050 °C complete conversion of CO₂ into CO must take place (when there is enough time for equilibrium coming).

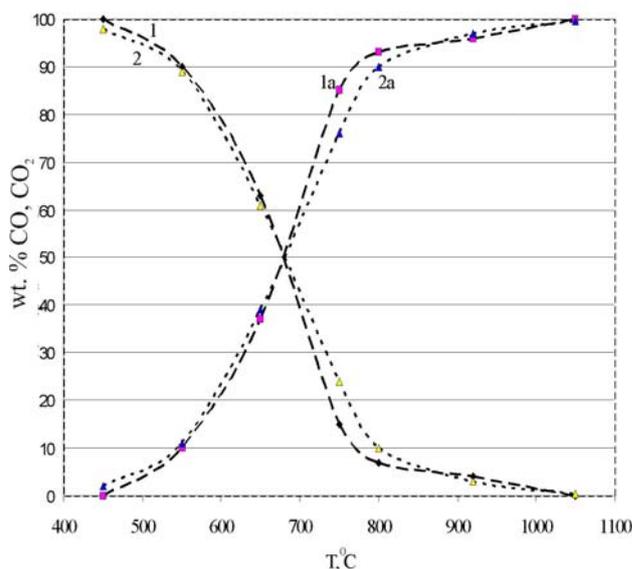


Fig. 1. Dependence of generator gas composition upon temperature (1 – experimental data of CO₂ containing in generator gas at generator outlet; 2 – calculated data of CO₂ containing in generator gas; 1 a – practically obtained data of CO containing at generator outlet; 2 a – calculated data of CO formation).

From the presented Fig. 1 it is obvious that under temperature being above 850 °C practically total conversion of CO₂ into CO occurs. To reduce the time of obtaining generator gas with high reducing qualities when the part of carbon monoxide approaches to 100 %, it is desirable to carry out the process under temperature being not below 800 °C. The presented data must be considered as a limit to which gas composition tends by solid fuel gasification. It should be noted that the time of oxidant contact with a fuel depends

upon fuel type and in every case it is necessary to approach individually the parameters of the process carrying out. Heat supplying uncovers extra opportunities to obtain reducing gas from low-energy fuel and also from fuel mixtures of high moisture content. In the last case the proceeding of endothermic reaction of water conversion with hydrogen obtaining is possible. The given phenomenon takes a positive effect on the proceeding of both oxides reduction and their cleaning from hydrogen deposition in connection with reversible Boduar reaction proceeding.

In going to reduction processes the special attention is paid to timely and total removal of residual water steam out of reaction volume. It made it possible to carry out the correlation of reduction time depending upon the composition of gas being within reaction zone.

It is important to use repeatedly carbon dioxide which is redirected to gas generator where its interaction with carbon-containing raw material takes place. It permits to design the closed-circuit cycle of carbon raw material using and make the process of hydrogen obtaining to be more ecologically pure. Carbon dioxide which forms after magnetite reduction will not be thrown into the air but will be directed repeatedly out of reaction zone by turbopump into the generator of reducing gas where it is necessary to create thermodynamic conditions, for its interaction with carbon or other carbon-containing materials for forming carbon monoxide. When the specified conditions are satisfied the gaseous components (CO , CO_2) of reduction process will be put on reversible cycle and the given stage will proceed practically without emission of ecologically hazardous compounds into the air.

In the process of the proceeding of repeated many times oxidation-reduction (redox) cycles for hydrogen obtaining it is necessary to have the data concerning the change of kinetic parameters and properties of materials functioning over a long period of time under conditions of CO and water steam at a temperature $800\text{--}1000\text{ }^\circ\text{C}$ without their drawing from the reactor working zone. Kinetic data of reduction stages under non-isothermic and isothermic temperature conditions and conditions of pure carbon oxide and also oxidation degree of iron reduced by water steam in the stage of hydrogen obtaining are presented in the Fig. 2.

The increase of reaction zone temperature with the rate of $14.3\text{ }^\circ\text{C}/\text{min}$ is demonstrated in the Fig. 2 (c. 5) at the first cycle of Fe_2O_3 reducing

stage (c. 1). The reduction has been carried out by temperature increase up to $850\text{ }^\circ\text{C}$ and its decrease down to $800\text{ }^\circ\text{C}$ at the stage of iron oxidation by water steam. The point "a" determines the coordinates where steam supply takes place. Under the pointed rate of temperature increase the process of reduction starts under temperature above $460\text{ }^\circ\text{C}$.

Under $\alpha \cong 34\%$ and $600\text{ }^\circ\text{C}$ reduction rate retards. In the given temperature range the change of the reduction process mechanism takes place from low-temperature one (up to $570\text{ }^\circ\text{C}$) passing over Fe_3O_4 transformation to high-temperature process ($\text{Fe}_2\text{O}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}$).

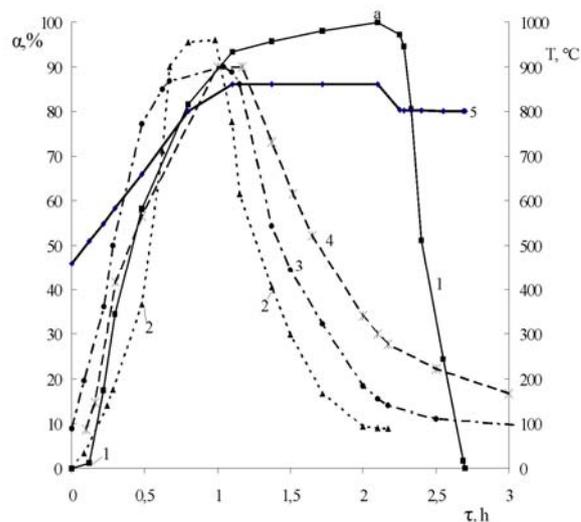


Fig. 2. Dependence of Fe_2O_3 reduction degree in CO and oxidation degree of reduced iron by water steam at the stage of iron obtaining upon time, temperature and number of cycles (1 – the first cycle under temperature of non-isothermic reduction along the curve 5; 2 – the second cycle, $800\text{ }^\circ\text{C}$; 3 – the third cycle, $820\text{ }^\circ\text{C}$; 4 – the fifth, $900\text{ }^\circ\text{C}$).

Conclusions

By the carried out investigation the opportunity has been proved to obtain hydrogen by iron-steam method in no less than 6-7 cycles, during which chemical activity of the working mass consisting of the mixture of metallurgic scale waste decreases slightly.

To increase the number of effective cycles of reduction and oxidation it is necessary to follow closely thermo-chemical and technological parameters of the two stages of the process of hydrogen production.