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APPLICATION OF THE DIVIDED METHOD REAGENTS TO RESEARCH OF HETEROGENEOUS PROCESSES IN METALLURGY

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For express-research of mechanism and kinetics of heterogeneous processes including the interaction of two and more solid reagent there is worked out the method of the separated reagents. With use of this method a process of chlorinating for magnesite there are investigated and improved and also the process of carburization of iron oxide reagents and metal-carbon compositions has been studied.

Keywords: heterogeneous process, mechanism and kinetics, reactor, reagent, magnesite, iron oxide, speed of process

Introduction. At implementation of technological developments at the coloured and black metallurgy, chemical technology and other areas achievement of optimal organization for technological processes and maximal economic efficiency of production possible only on the basis of the use of the set mechanism of heterogeneous chemical transformations flowing in the system. When in the zone of reaction 3-4 and more than reagent (hard, liquid, gaseous) simultaneously present and co-operate, for optimal organization of process it is necessary to set a mechanism and consistency of physical and chemical transformations flowing in an apparatus. On the basis of this knowledge it is possible to define speed of flowing binary reactions, to study their kinetics, to distinguish the most rapid and slow stages, limiting a process, and to organize their flow and apparatus registration so that high speed of total heterogeneous process and burst productivity of technological apparatus will be attained.

The processes of chlorinating of mineral raw material and concentrates of rare metals, restoration melting, oxidizing burning, lixiviating, heterogeneous catalysis, processes of blast furnace production of iron, making converter and martin production of steel etc behave to the similar heterogeneous processes.

Analysis of applicability of the known methods of research. The methods of study of kinetics for chemical reactions differ by depth mathematical working, however there are applicated mainly for description of binary reactions. So the known method of successive reactions [1] we will apply for a study transformations of reagent A in the product P through an intermediate product B: $A \Rightarrow B \Rightarrow P$. However it can be used for research of the difficult multicomponent systems (charges) in which can flow simultaneously a few processes, including in various directions.

Other known methods, based on fixing of speed of feed motion of reactionary surface of interphase [2], or on the construction of morphological models of formation and height of embryos [3], also more applicable for the construction of theoretical models, than for raising of experiment at the study of multicomponent charges.

Experimental researches of kinetics of processes on the basis of the use of methods of onefactor, fractional factor and complete factor analysis [4] though got wide distribution, however on the basis of the got results it is possible to do only indirect (hypothetical) conclusions about the mechanism of process, consistency of flowing transformations in the system, speed of one or another stage.

Substantiation of requirements to the new practical method of research. With the purpose of removal of the indicated limitations at research of processes of chloromagnesium raw material receipt for the electrolytic production of magnesium [5] it was set the problem of development of method, allowing by organization of the minimum quantity of experiments to get information about a mechanism and speed of flowing chemical transformations in the multicomponent systems (charges) and on this basis to realize maximally effective technology.

Usually at research of speed of heterogeneous processes, including co-operation two and more than hard, and also liquid or gaseous reagents, loading of hard reagents in a reactor is carried out in the mixed or briquette state.

Worked out method [6], consists in that before the beginning of research hard reagents (two or more) are placed in separate reactors or in one reactor, but separately (by layers) with use of permeable partitions. Liquid or gaseous reagents in mixture or by turns give in a reactor (or in the consistency of a few reactors), and they consistently co-operate at first with one hard reagent, after with other etc. During realization of experiment in the volume of one reactor the contact of all reagents is provided and possibility of flowing of retroactions is not eliminated. In every experiment on expiration of set its duration there are take away the test of the got product and after its analysis expect speed of process of co-operation on the output of the finished product. Changing the consistency of location hard reagents in a subsequent experiment, we change periodicity of the flowing stages of process and, the same, its total speed. Serve of liquid or gaseous reagents in a reactor it is possible to carry out simultaneously at their different correlations, or by turns, the input of intermediate products or other reagents, not participating in an initial process is including possible.

On the basis of row experiments with the different consistency of location of hard reagents or with the change of composition of liquid (gaseous) reagents it is possible to make conclusion about speed of the separate stages, mechanism of process and its optimal technological appearance.

Example of the use of the worked out method. A method is practically used for the improvement of technology for receipt of magnesium chloride from magnesite in mine electric furnaces as follows.

The before existing industrial process of chlorinating for magnesite in electric furnaces included the use in composition the charge of hard reagents – caustic magnesite (oxide magnesium) and repairer (pitch or oil coke). The process of preparation of charge included the stages of breakage of reagents, their grinding, mixing of components, briquetting, drying and burning of briquettes', and the process of their chlorinating by gaseous reagents (by chlorine-air mixture) was only then carried out in electric furnaces [7].

It was accepted to consider that basis of process of chlorinating of briquetes is made by the heterogeneous process of co-operation of oxide magnesium with a chlorine in presence a hard repairer, described by reactions:

$$MgO + Cl_2 + C \Leftrightarrow MgCl_{2(p)} + CO, \quad \Delta H = \text{ - 128.3 kJou/mol} ; \tag{1}$$

$$2MgO + 2Cl_2 + C \Leftrightarrow 2MgCl_{2(p)} + CO_2, \quad \Delta H = \text{ - 394.7 kJou/mol} . \tag{2}$$

Their equations over of reactions characterize a total process which really flows at a few successive stages.

For more thin research of conformities to law of mechanism and kinetics of process of chlorinating researches conducted on the basis of the worked out method of the divided reagents were carried out.

In the first series of experiments there were carried out tests on chlorinating with the division of repairer and oxide magnesium and placing of them in separate reactionary vessels (fig. 1). In a quartz reactor 1 with a diameter a 40 mm, set in mine electric furnace, in chloride fusion loaded the sample of oil coke, and in an analogical reactor 2 – sample of magnesite. A chlorine was given in a reactor 1, and going out a reactor gases were given in fusion of reactor 2 on chlorinating of magnesium oxide. Fusion was prepared from the chlorides of potassium and sodium of brand of chemical cleanness, chloride of magnesium - by the meltback of condensate chloride magnesium. Total mass of fusion made a 160.0 g, initial content $MgCl_2$ in fusion – 10 %, mass correlation of KCl : $NaCl$ = 5:1. The temperature of fusion was supported by 800 ºC. Mass of the loaded sample of caustic magnesite of Satka deposit (the masses. stake, %: MgO – 96.5) made a 20.0 g, oil coke of brand КЗ-0 (ГОСТ 22898-78) – 10.0 g. In tests magnesite of faction by 0.071-0.10 mm and oil coke of factions 0.10-0.16 mm are used.

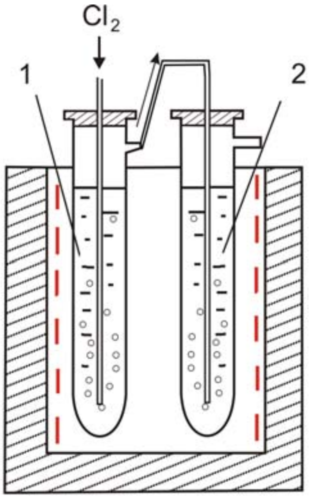

Figure 1 - A chart of experiment with the division of magnesium oxide and repairer in separate reactionary vessels

There are used liquid chlorine on ГОСТ 6718-86, oxygen - from bulbs on ГОСТ 5583-78, carbon dioxide - on ГОСТ 8050-85. A dosage and control for expense of gases was produced by a plastometer method. Duration of experience was

30 minutes. Speed of chlorinating was determined by a calculation way on the change of content $MgCl_2$ in fusion, measuring of content $MgCl_2$ produced by trilonometric method.

In the first test, chlorinating was carried out at a serve of chlorine in the reactor 1, the expense of which made 20 dm^3/hour. Thus in a reactor 2 speed of chlorinating made a 2.3 ± 0.3 g MgO/hour. In the second test oxygen in the volume of 10 dm^3/hour was added to the chlorine, that entailed the increase of speed of chlorinating in a reactor 2 a to 5.4 ± 0.5 g MgO/hour. In the third test dioxide of carbon (10 dm^3/hour) was added to the chlorine, that brought to the height of speed of chlorinating in a reactor 2 a to 7.4 ± 0.6 g MgO/hour.

Appreciable speed of chlorinating in the first test is attained, obviously, due to pyrolysis of oil coke and participation in the process of chlorinating of volatile, components the mass stake of which in oil coke arrived at 6.5 %. Increase of speed of chlorinating at dilution of chlorine by oxygen or carbon dioxide, obviously testifies about gasification of hard repairer in a reactor (1) on reactions

$$2C + O_2 \Leftrightarrow 2CO, \quad \Delta H = -246.62 \text{ kJou/mol}; \tag{3}$$

$$C + CO_2 \Leftrightarrow 2CO, \quad \Delta H = 162.53 \text{ kJou/mol} \tag{4}$$

and about the further flowing of process of chlorinating in a reactor 2 with the use of carbon oxide as an acceptor of oxygen of on a reaction

$$MgO + Cl_2 + CO \Leftrightarrow MgCl_{2(p)} + CO_2, \quad \Delta H = -267.15 \text{ kJou/mol}. \tag{5}$$

The got results, nevertheless, do not give a synonymous answer, what from the stages of chlorinating process, at simultaneous introduction of hard repairer and oxide magnesium at electrical furnace, is primary, what stage limits a process.

The second series of experiments were conducted in a quartz reactor with diameter a 45 mm, set in mine electrical furnace, in the underbody of which during a process on a quartz tube with a diameter 5 mm gave gas reagents (fig. 2).

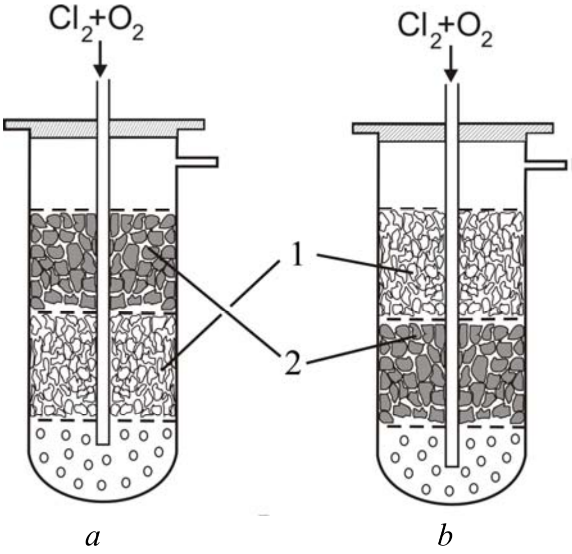

Figure 2 - A chart of experiment with the division of oxide of magnesium and repairer is in one reactionary vessel: 1 is a magnesite; 2 is a charcoal.

Originally in a reactor separately the burnt magnesite and repairer (charcoal) of faction a 2-7 mm loaded which in a reactor were divided by permeable partitions from fluorine phlogopite. Mass of magnesite sample was equal a 20.0 g, mass of sample of repairer – 11.6 g. After building-up in the reactor of chloride fusion ($KCl : NaCl$ = 5:1) by mass 120 g, a temperature in a reactor was lifted to 800 ºC and began the serve of gaseous reagents. The expense of chlorinating gas was supported 30 dm^3/hour at correlation of $Cl_2 : O_2 = 2:1$, duration of experiment made 30 minutes. Then sample of the prochlorinated fusion took away, analyzed on content $MgCl_2$ and calculation way determined speed of process of chlorinating.

For determination of speed of process at varying of its stages two experiments are conducted. In the first test (fig. 2.a) chlorinating gas originally passed through the layer of magnesite, where the reaction of chlorinating flowed

$$2MgO + 2Cl_2 \Leftrightarrow 2MgCl_{2(p)} + O_2 \ , \qquad (6)$$

and then through the layer of coal, where renewal of the distinguished oxygen was on a reaction (3). Speed of chlorinating here made a 1.8 ± 0.3 g MgO/hour.

In the second test (fig. 2.b) the consistency of location of hard reagents was changed. Chlorinating gas originally passed through the layer of coal, where gasification of repairer was on a reaction (3), and in the layer of magnesite the process of chlorinating MgO was carried out with the use oxygen as an acceptor for carbon oxide on a reaction (6). Speed of chlorinating here increased a to 4.8 ± 0.5 g MgO/hour.

On the basis of results of the conducted tests conclusion made that maximum speed of chlorinating process and output of the finished product – dichloride of magnesium, can be attained at primary realization in the reactor of the stage of gasification of repairer. Therefore for optimal organization of technology, taking into account subzero wettableness of carbon chloride fusions [8], gasification of hard repairer was distinguished in the separate preliminary technological stage and carried out in a separate apparatus [9].

Further development and application of method. Method of divided reagents is simple enough and effective universal experimental instrument, and can be recommended for research of processes of co-operation, flowing in the most various heterogeneous systems.

So for research of process of carburization of ferrioxide reagents and receipt of metalcarbon compositions also of this method was used. Metalcarbon compositions, got in the process of thermocatalytic disintegration of carboncontaining gases, in particular, carbon monooxide on catalysts from the group of iron, are of interest as carboncontaining raw material for the row of areas of technique. It is assisted extraordinary morphology of material, presence of close connection between the fine-dispersed metal and carbon, and also possibility in a wide interval to vary correlation carbon and metallic making [10].

Researches were executed with the use of chart that it is given on fig. 2, with the division of iron oxide 1 and repairer 2, where instead of mixture of $Cl_2 + O_2$ werw applied mixture of $CO + CO_2$. Originally in a reactor separately samples of iron oxide Fe_2O_3 by mass 30.0 g and repairer (charcoal) of faction 2-7 mm by mass

15.8 g loaded which in a reactor were divided by permeable partitions from fluorine phlogopite. A temperature in a reactor was lifted to 950 ºC and began the serve of gaseous reagents ($CO + CO_2$). The expense of mixture of gases was supported 35 dm^3/hour at correlation $CO : CO_2 = 3 : 2$, duration of experiment made 60 minutes. After sample of carburization product took away, analyzed on content of carbon and a calculation way was determine speed of process of carburization.

For determination of speed of process at varying of sequence for its stages two tests are conducted. In the first test carbon containing gas mixture originally passed through the layer of oxide of iron, where the ordinary reaction of renewal flowed

$$Fe_2O_2 + 2CO \Leftrightarrow 2Fe + 2CO_2 \ , \tag{7}$$

and then through the layer of coal, where Ball-Buduar reaction (4) was. Speed of process here made a 2.6 ± 0.3 g Carbon/hour.

In the second test the sequence of location of hard reagents was changed. Reactionary gas originally passed through the layer of coal, where gasification of repairer was on a reaction (3), and the process of carburization Fe_2O_3 was carried out in the layer of iron oxide. Speed of carburization here increased a to 7.8 ± 0.5 g Carbon/hour.

On the basis of results of the carried out experiments conclusion made that maximum speed of carburization iron process and output of the finished product is mefalcarbon compositions, can be attained at primary realization in the process of the stage of gasification of repairer.

Conclusions. As a result of the use of method of the divided reagents by realization of the minimum quantity of experiments got taking about the mechanism of process of chlorinating and speed of its separate stages. On their basis optimal organization of technology is carried out and the apparatus-technological chart of preparation of hard reagents is substantially simplified to the process of chlorinating – all preparatory technological operations are removed, except for breakage (seven reparations are reduced). Specific volume speed of process of chlorinating on the pilot setting is megascopic in three times, as compared to attained in electrical furnaces. In transition to industrial realization of process it allows to increase the productivity of reactor (chlorinator) of the same sizes in three times, substantially to shorten capital costs and lower the prime price of the got chloride of magnesium and producible from its magnesium. A method also is successfully used for determination of conditions of achievement of maximal speed of carburization of ferrioxide reagents at the receipt of metal-carbon compositions.

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