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AUTOCLAVE DTA APPLICATION IN TECHNOLOGICAL RESEARCHES

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ABSTRACT

Data basing the investigation method of heterogeneous systems in hydrothermal conditions by the autoclave DTA method are listed. Concrete investigation results are given.

EXPERIMENTAL

As far as the autoclabe processes are finding wide application in the processing technology of different raw materials, it is necessary to record the data on varying reaction parameters in direct autoclave environment. The high sensibility of differential thermocouple and its possibility of direct introduction into the reaction environment let the DTA method be used in the main for studying autoclave process.

Having this for an object we worked out a simple and reliable plant for using DTA method by high pressures up to temperatures 623 K/1/. The main units of the plant are the autoclaves - the sections with 1,5-5,0 cm^3 in volume made of metal which is stable in the given environment, a furnace with program temperature regulation and a recording block. The thermocouples are either introduced directly intp the reactioning region or are covered by the jacket, comprising a single whole with an autoclave cover and its thickness is 0,3-0,5mm, while the diameter is 2,3 mm. The autoclave tightness is got by using the special gasket that makes possible the recording of thermal analysis curves at the redundant pressure in the reactor with the sufficient accuracy up to 100 kg/cm^2. We managed to keep up the satisfactory level corresponding to the declination 0,7 K/cm. The area thermal efficiency is 0,2 /J/K·a

A solid sample is usually placed for investigation into one of the autocalaves with the amount of 0,1-2,5g which is then filled up by the given solution in such an amount that the autoclave free

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space would be 20-25%. The annealed aluminium oxide or specific water suspension is charged into another one as a standard, then the autoclaves are sealed off, put into the thermoblock and subjected to uniform heating at the given rate (0,03- 0,27K/s) with thermoanalysis curves recording.

RESULTS AND DISCUSSION

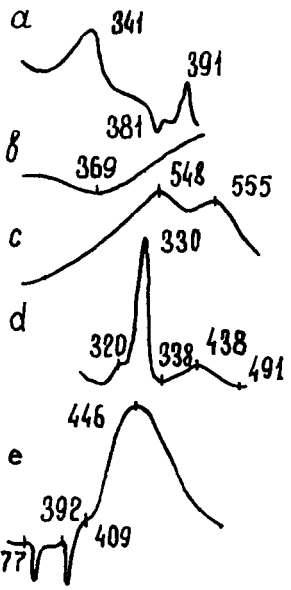
Investigation results of the crystal sulphur, selenium and tellurium interactions with natriumhydroxide solutions (2,0+15,7M) by using autoclave DTA method are given in this article. A number of characteristic thermal effects on chalcogen suspension heating curves is observed; it is caused by the fact that it has been determined by the application of the other physicochemical methods (X-ray-phase, DTA of solid phases, electron spectra and chemical). This permitted to determine thermal and kinetic processes parameters.

It is found that sulphur dissolution products in the alkaline solution (mass ratio sulphur and solution from 1 to 1) are polysulphide and thiosulphate ions; the process is characterized by exoeffect at the temperature range 349-330 K (with concentration change up to 2,0-15,7 M). At 381°K (see the Fig.) sulphur melts at the autoclave with the following supplementary dissolution of the fused sulphur with the rate increasing ion sulphide polysulphurizing. ΔH values of dissolution reaction increase with rising of alkali concentration from 2,2 to 10,2 Kj/mol and activation energy value, found from DTA data by /2/ decreases from 79,6 to 48,6 Kj/mol.

The base product of Se_{hex} with natriumhydroxide solutions interaction is amorphous selenium in high-dispersed form; this effect is recorded on DTA curve at 369 K (see the Fig.) According to DTA data the enthalpy value of interaction between Se_{hex} and alkali solutions is equal to+4,7 Kj/mol. This value is practically in agreement with ΔH value of reaction $Se_{red\ amorphous} \rightarrow Se_{hex}$ (+4,9:-5,4). The process activation energy which is equal to 137,9 ±6,7 Kj/mol and is not dependent on alkali concentration indicates the process mechanism invariability.

The crystal tellurium contacting with alkali solution is defined by double exothermic effect, the maxima of which are close when NaOH concentration is increased. This is connected with the

peculiarities of tellurium dissolution resulting telluride - and tellurite-ions.



The Fig. The DTA curves showing the interaction of sulphur (a), selenium (b), tellurium (c), silicon (d) with natrium hydroxide solution and the sulphuric oxide sulphurizing curves.

The DTA method results were confirmed by especial isothermic experiments in autoclave; thus Eact-values of chalcogen dissolution were 102,7 and 96, 4 Kj/mol for sulphur and 104,8 and 99,7 Kj/mol for silver (for 2,0 and 5,0 M NaOH -solutions respectively). During DTA method studying of elementary chalcogen interaction with copper powders and silver powders in alkali solutions the analogous data were obtained. The above mentioned investigations allowed to disclose a number of behaviours being valuable for practical development of selenium and tellurium recovery from chalcogen containing raw technology.

Autoclave DTA method can be also successfully used for studying of heterogeneous processes under conditions of active gas evolution. For instance, DTA curve fixes solution exoeffects at 330, 438 K at silicon dissolution in caustic natrium solution with hydrogen evolution (see the Fig.)

According to DTA and chemical analysis data the obtained enthalpy (330 Kj) of the process is in good agreement with the theoretically calculated one. The obtained DTA and isothermic kinetic values of the process activation energy of 60-73 and 56 Kj/mol, respectively represent the kinetic limits in dissolution process.

Given method is very convenient for specific technology problem solution connected with autoclave processes. The authors carried out researches which permitted them to choose optimal conditions to refine barite and Zn concentrates from quartz; they investigated the problem connected with metal oxide compound-sulp-

phide transitions; in some cases it is very important for production processes. Autoclave DTA method permitted to obtain comparatively mild Cu oxide mineral sulphurizing conditions. Figure (e) shows DTA curve of quantitative Cu (1) oxide sulphurizing in water solution.

The cited examples illustrate the wide possibilities in technological researches; knowledge of different parameter effect on temperature, shape and thermal effect area may give us important information about mechanism and thermochemical and kinetic parameters in autoclave processes. The authors showed that mathematic planning of experiment promotes more reliable results.

LITERATURE

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