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ECOLOGICALLY SAFETY STORAGE OF HIGH-SULFUR COAL WASTES AND TECHNOLOGIES OF THEIR PROCESSING

ЭКОЛОГИЧЕСКИ БЕЗОПАСНОЕ ХРАНЕНИЕ ВЫСОКОСЕРНИСТЫХ УГЛЕОТХОДОВ И ПРОЦЕССЫ ИХ ПЕРЕРАБОТКИ

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Abstract. *There are shown the data on composition and technological properties of solid wastes with high sulphur contents after coal mining and preparation (SCWHS) in Russia.*

The natural processes causing the pollution of the environment due to contents of sulphur and some potentially toxic elements in these wastes are considered. However these wastes may be promising as raw materials for producing some saleable products. According to Russian regulation a payment for wastes storing depends on so called their class of danger (CD). Methods for the CD determination for coal wastes are described.

Results of simulating of thermal treatment in different conditions of SCWHC are shown. Using these results some processes of SCWHS utilization are proposed to produce some valuable products.

Some new criteria based on Russian regulations are worked out to determine an ecological danger of mine waters of Russian enterprises and promising methods of mine waters cleaning and utilization.

There were conducted experimental investigations on the localization of ecologically dangerous products forming due to interaction of SCWHS with waters flowing through SCWHS damps. Some carbonate rocks and fly ashes were tried for this purpose. There were found that the localization is occurred due to forming of new minerals along with a delaying of the oxidation of sulphides containing in SCWHS. Using these results grounds of some methods are proposed to decrease concentrations of ecologically toxic elements (Fe, Al, Ni, Cu, Cr, Zn, As, Pd und oth.) till values considerably less than permitted ones in waters flowing through SCWHS damps. New promising results of experiments on laboratory and industrial installations were got for using these technologies with carbonate rocks for enterprises in central Russia.

Keywords: *solid wastes with high sulfur, technological properties, utilization, thermal treatment, localization of ecologically dangerous products.*

Introduction

Coal wastes designated as SCWHS with relatively high contents of sulfur ($S^d_t > 1.5\%$, mass.), in some cases organic substances ($C^d_o > 12\%$) and toxic trace elements are piled in huge dumps at some enterprises after mining or preparing of sulfurous coals ($S^d_t > 1.5 - 2\%$), for example in Russia (Moscow and oth. basins). One of the most serious environmental problems associated with the surface disposal of sulfur-bearing wastes is the oxidation of the inherent pyrite and the generation of acidity with solubilization of compounds of some elements contained in wastes and toxic to the environment, e.g. the generation of hazardous coal mine drainage and subsequent contamination of surface streams and underground waters. Main reactions are the following:

$$FeS_2 + H_2O + O_2 \rightarrow FeS\ x + H_2SO_4 + Fe_2(SO_4)_3 + Fe\ SO_4 \qquad (1)$$

$$MS + O_2 \rightarrow MSO_4 \qquad (2)$$

M - Co, Ni, Pb, Zn

$$H_2O + E_2S_3 + O_2 \rightarrow H_3EO_3 + H_2SO_4 + SO_2 \qquad (3)$$

E - As, Sb

$$MeCO_3 + H_2SO_4 \rightarrow MSO_4 \qquad (4)$$

Me - Mn, Sr, Pb, Zn, Cr

There were conducted investigations on the localization of ecologically dangerous products forming due to interaction of SCWHS with waters flowing through SCWHS damps. Some carbonate rocks and fly ashes were tried for this purpose. There were found that the localization is occurred due to forming of new minerals along with a delaying of the oxidation of sulphides containing in SCWHS. Using these results grounds of some methods are proposed to decrease concentrations of ecologically toxic elements (Fe, Al, Ni, Cu, Cr, Zn, As, Pd and oth.) till values considerably less than permitted ones in waters flowing through SCWHS damps [1-5]. New promising results of experiments on laboratory and industrial installations were got for using these technologies with carbonate rocks for enterprises in central Russia.

Materials and methods

There were used samples picked at some dumps of the Moscow lignite basin where solid wastes with S^d t = 1.5 – 9% are stored drainage waters from them have pH = 3.1 – 3.8. Besides and concentrations of some hazardous trace elements (Zn, As, Se, Cr and some others) are sometimes more than permitted ones [1]. These wastes contain coal organic substances (C^do=12-28%), which may cause dangerous ecological consequences but is favourable for their utilization.

According to experimental investigations conducted dangerous actions of SCWHS on the environment may occur in a noticeable degree if their sulphur content is > 1.5 - 2%.

It have been found that these dangerous actions on the environment may be decreased till acceptable levels while mixing SCWHS with substances, for example limestone or dolomite neutralizing H_2SO_4 [2,3]. This method have been tried on dumps of SCWHS situated in Moscow lignite basin where have been accumulated nearly 100 mln.t of SCWHS in dumps and slurry ponds.

The experimental plot (64 square meters) was constructed at a distance of 20 meters from the dump of Vasilevskaya mine situated in the most populated district. It was divided into four equal parts which were separated from each other with waterproof partitions.

Each part contains SCWHS taken from the dump. Their average sulfur content was 3.5% and A^d = 72.4 %. The limestone using for mixing was from the local enterprise. It was crushed till < 3 mm and contained near 95 % of $CaCO_3$. The external side of the plot is enclosed with a wooden wall. The wastes are put on waterproof film that is sloping towards the centre. So all waters from the each section are filtered and go to a special collector where they were measured and taken for the analyses. Each part of the experimental plot contains different amount of limestone added to the wastes: 0, 10 and 20% of limestone.

Analysis of chemical composition of water, filtrating through high-sulfur coal wastes with different additions of limestone which contains in different parts of experimental plot, allowed defining the main tendency of its alteration depending on time [4]. Approximately 36 charts were build which describe the considerable influence of limestone additions on composition of filtrating water.

Methods of thermodynamics simulation, experiments on thermal treatments of initial samples or their mixtures with $CaCO_3$ along with chemical and X-ray analyses of got residues were applied to find technologies of SCWHS utilization.

Results and their discussion

Some results of experimental investigations on chemical compositions of waters filtering through initial SCWHS and their mixtures with $CaCO_3$ stored in above mentioned plot are shown on the Table 1 and Fig.1–3.

The results of the experiment, confirmed the main suppositions and results of laboratory tests. The important reduction of «acidity» of water along with concentrations of toxic elements in them is observed. So the ecological safety of the dump storing SCWHS may be achieved with this method.

Table 1.

The comparison of some trace elements concentrations in waters filtered through coal wastes without limestone additions

№	*Element*	*Concentration,10^{-6} g/l*	*Permitted concentration, 10^{-6} g/l*
1	Al	60 000	500
2	V	275	200
3	Mn	1 600	200
4	Co	2 500	1000
5	Ni	2 500	200
6	Cu	1 200	200
7	Zn	14 000	2 000
8	Cd	62	1
9	Hg	2,75	0,5

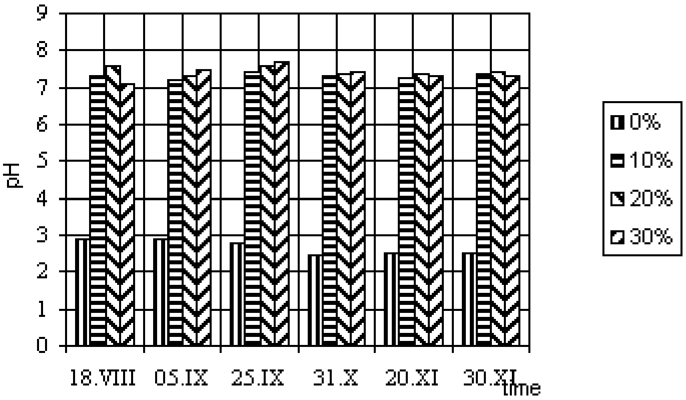

Fig. 1. **pH values in waters from different parts of the plot**

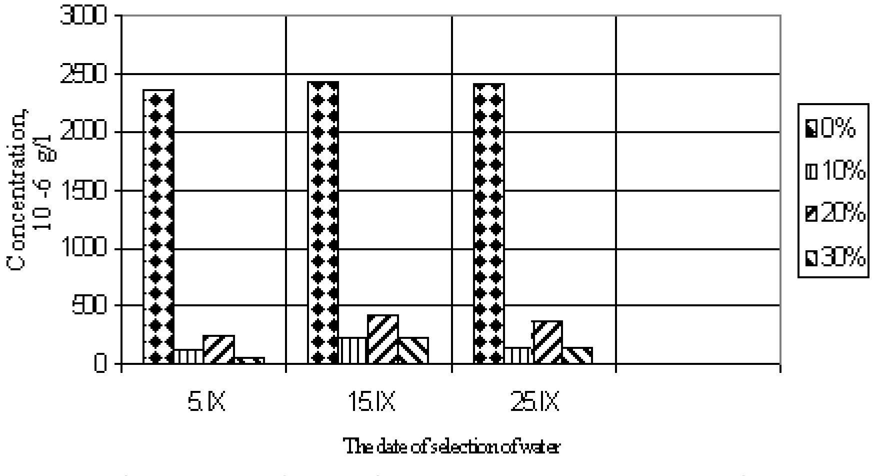

Fig. 2. **The change of quantity of Ni in filtrated trough the parts of experimental plot at «Vasilyevskaya» coal-mine**

The utilization of such wastes with traditional methods isn't possible practically due to high S contents. Two different thermal methods were investigated to solve this problem:

- the thermal processing of initial wastes with passing of S in gas phase, H_2SO_4 producing from sulphur oxides and obtaining some valuable products from solid residues after thermal processing;
- mixing SCWHS with limestone, thermal processing of got mixtures with quantitative passing of S in solid residues which may be used as binding materials.

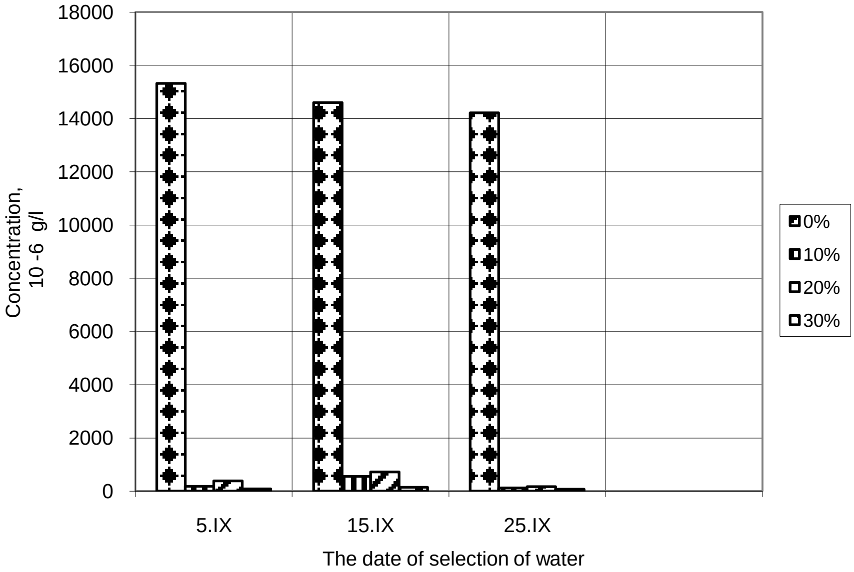

Fig. 3. **The change of quantity of Zn in wastes filtrated through the parts of experimental plot at «Vasilyevskaya» coal-mine**

Authors have investigated both thermal methods with the method of thermodynamic simulation [5] and experiments at bench and pilot installations.

The thermodynamic simulation was conducted for reduced and oxidizing atmosphere and allowed to evaluate qualitatively contents of all products which formed in considered heterogeneous systems in the equilibrium states. During this simulation all probable transformations of the initial wastes and additives were taken into consideration.

According to the thermodynamic simulation the main components of the gaseous phase (at the coefficient of air excess (α) =1.2) over a temperature range 25-1400°C are (% by volume): N_2 (72-74%), CO_2 (14.3-14.75%) and H_2O (8.6-8.9%). Thermal processing at elevated temperatures, between 500 to 1400°C, increases slightly the oxygen content (from 2.4 to 3.39%). The concentration of sulfur dioxide is about 2.5 x 10^{-3} % up to 450°C and increases with temperature to 0.8 x 10^{-2} at 500°C and to 1.7% at 700°C. However, as temperature increases from 700 to 1400°C, SO_2 concentration increases very slowly up to its maximum value of about 2%.

As temperature rises from 100 to 1100°C, there are in solid phases following compounds with a concentration >10^{-4} % kg/kg : SiO_2, $3Al_2O_3{\cdot}2SiO_2$, $Al_2O_3.SiO_2$, Fe_2O_3, and within a narrow temperature range $Al_2(SO_4)_3$ (up to 600°C), $CaSiO_3$ (>950°C), MgO (>850°C), FeO,Fe_3O_4 (>850°C), $FeSO_4$ (up to 700°C) and $Fe_2(SO_4)_3$ (up to 650°C). The concentration of iron-bearing compounds during thermal treatment over the entire temperature range when a=1.2 is shown on the Figure 4.

As seen from these data, when a reaction reaches equilibrium in a closed system, iron-bearing compounds are a mixture of $Fe_2(SO_4)$ and Fe_2O_3 admixed with FeO, Fe_3O_4 and $FeSO_4$. At the same time the content of iron sulfates decreases sharply at temperatures higher than 450 and the content of iron oxides increases at temperatures higher than 600°C. It has to be mentioned though that if thermal treatment is conducted in an "open" system, gaseous products are removed continuously and substantial changes in composition of the end products may be occurred. In this case the concentration of FeO or Fe_3O_4 produced by reactions 5.6 and 9 may be higher than that predicted for the equilibrium state.

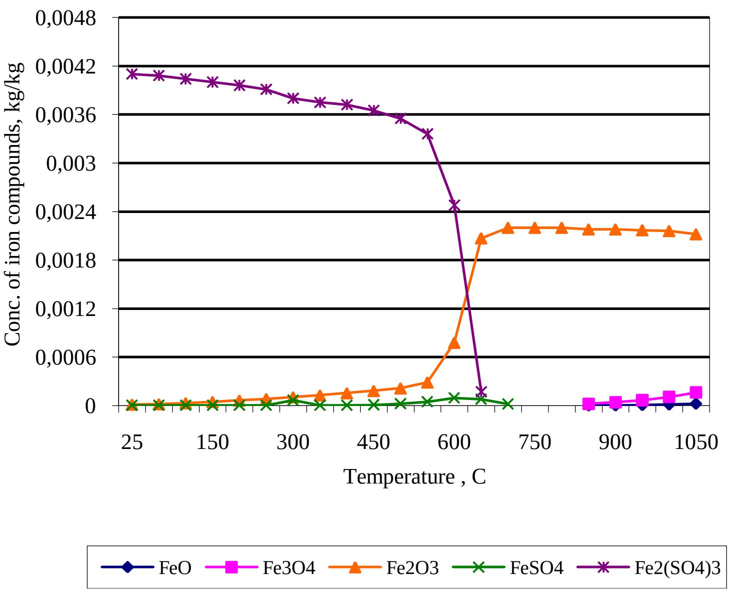

Fig. 4. **Thermodynamic simulation of the composition of iron compounds during thermal treatment of SCWHS at α =1.2**

All amounts of sulfur are in gaseous phase as SO_2 nearly at temperatures > 900 C.

During thermal processing with α=0.6 it is expected a larger number of compounds presenting in gaseous and condensed phases at concentration above 10^{-4}%. Over a temperature range 550-850°C the components of the gaseous phase are (by volume %): N_2 (61.9-61.3%), H_2O (8.8 to 9.2%); CO_2 (19.6 to 16.3%), CO (2.9 to 7.6%), H_2S (1.43 to 1.6%), H_2 (3.7 to 4.2%), SO_2, SO_3 (~ 0.0048%) and CH_4 (< 0.0026%). In the condensed phases some carbon may be presented with its content sharply decreasing from 0.36 to 0.003 kg/kg, as temperature increases from 550 to 850°C. The main components (with a concentration higher than 0.01 kg/kg) are: SiO_2, Al_2O_3, $3Al_2O_3 \cdot 2Si0_2$, $Al_2O_3 \cdot 2SiO_2$, MgO, TiO_2, $CaSiO_3$ and at temperatures higher than 650–700°C FeS, FeS_2, CaS and Fe are formed. So S is distributed between gaseous and solid phases.

The main iron bearing end products after thermal treatment at temperatures between 550-850°C with α =0.6 are FeS, FeS_2, FeO and Fe. When temperature increases FeS_2 decreases, FeS increases, reaches its maximum at 750°C and then decreases and FeO and Fe increase steadily. It is also seen that thermal processing in a reducing medium leads to the production of solid iron-bearing components (e.g. pyrotine, magnetite and α–Fe) with ferromagnetic properties.

So according to the thermodynamic simulation it is possible to realise SCWHS thermal treatment (without any additives) producing ecologically safe and probably saleable solid products and gaseous sulfur compounds (SO_2, SO_3) which can be extracted as H_2SO_4 quantitatively with method of the firm “Halder Topse” as it will be shown below [6].

Known assumptions used for the thermodynamic simulation of high-temperature processes do not provide high accuracy for predicting phase changes. In order to confirm theoretical conclusions, laboratory investigations regarding thermal processing of high-sulfur coal wastes were carried out.

In order to determine the composition of reaction products the effect of the following parameters was studied: temperature (600– 800°C), air excess coefficient, α: 0.1-1.4 and duration (0.5–2 hours) while thermal processing of SCWHS. Experimental results for the duration of 1h are seen in the Table 2. The data of experiments 7, 8 show the satisfactory reproducibility of results. The experiments 4 and 16 were conducted to estimate a time factor on the process.

The experimental results show that 90 % transition of sulfur compounds into the gaseous phase can be achieved at temperature range 600-800°C with α between 0.5 and 1.4.

Table 2.

Effect of thermal processing conditions on sulfur removal

№ of experiment	*Temperature, °C*	*Air excess coefficient α*	*Sulfur in solid residue %*	*Sulfur removal into gas phase U_s , %*
9	600	1.39	0.73	95.1
11	600	0.58	1.39	90.5
14	600	0.84	1.14	92.6
20	600	0.35	5.65	63.0
4	700*	0.62	0.75	95.5
5	700	0.14	4.54	62.8
6	700	1.46	0.82	94.7
7	700	0.58	1.15	92.5
8	700	0.58	1.18	92.2
16	700**	0.5	0.92	93.8
17	700	1.2	0.61	95.5
12	800	1.2	0.56	96.7
13	800	0.51	3.2	91.6
15	800	0.8	1.26	91.6

*Duration - 2h, **Duration - 0,5 h .

The extreme values of Us, (94-96%), were observed at 600°C (α = 1.39), 700°C (α = 0.62 and 1.2), and 800°C (α = 1.2).

The formation of sulfur gaseous compounds is ended after 0.5 h of thermal processing (exp. 4, 7, 8, 16) practically. The residual contents of sulfur in the final products do not exceed 1.0- 1.1%. The water paste of the treated waste have pH values close to neutral (pH = 6.5-6.9). Mixing the obtained residues with weak-acid solutions (pH 2-3) does not cause any formation of hydrogen sulfide or sulfur dioxide. Therefore the final product is considered as ecologically safe and can be stored in dumps without causing any environmental impacts.

Thermal processing with a smaller air excess coefficient (α < 1) tends to diminish the amount of gaseous sulfur compounds. For example, the value of Us drops to 62.8 % (700°C, α = 0.14) or 63% (600°C, α = 0.35). Hence, in order to achieve high conversion degrees of sulfur compounds into the gaseous phase (higher than 90 %), thermal processing should be carried out within a temperature range of 600-800°C with α greater than 0.6. The final selection of temperature and air excess coefficient depends on the intended use of the final solid residue. When thermal processing is conducted with a ranging between 0.5 and 1.0, the gaseous phase contains hydrogen sulfide and CO, the amount of which increases with decreasing the air excess coefficient. For the removal of sulfur compounds from the gaseous phase, as stated previously, hydrogen sulfide must be converted into a mixture of SO_2 and SO_3 by burning with α greater 1.0.

Volumes of SO_2 and SO_3 in gaseous products (Table 2) depend on sulfur and carbon contents in initial wastes: they are increased with increasing of the former and diminishing of the latter.

The principal flow diagram of process of thermal processing of coal waste presented in Fig. 7.

The amount of limestone mixed with SCWHS provided following molar rates: $CaCO_3$: S = 1,1-1,2 ; $CaCO_3$: SiO_2 = 1,2-2. Temperatures of sintering 800-1000 C, and 0,5-1,5 hours. Parameters of a real process to transform all amounts of sulfur to $CaSO_4$ may depend on kinetic factors. So experiments were conducted to obtain optimal parameters of this process (Table 3).

Main results are shown on Figures 5, 6. All sulfur contained in SCWHS passes in solid residues practically after thermal processing at optimal conditions. However there were obtained in some experiments CaS, e.g. the compounds which forms H2S while those residues storing and it is undesirable for their utilization. Amounts of CaS are decreased with increasing of temperatures, durations of thermal processing, limestone amounts in initial mixtures.

For example, CaS amounts is decreased considerably after thermal treatment at 8000C of mixtures if limestone contents in them is increased from 20% till 40% or time of the thermal processing is grown from 0.5 till 2 hours.

Table 3.

Conditions for thermal processing of mixtures of SMSW with different $CaCO_3$ contents

Conditions of thermoprocessing		*Marking of samples after thermoprocessing*		
Temperature, ^{0}C	Time, min	30% $CaCO_3$	40% $CaCO_3$	50% $CaCO_3$
800	30	Z4	Z5	Z6
	60	Z7	Z8	Z9
	120	Z10	Z11	Z12
900	30	Z13	Z14	Z15
	60	Z16	Z17	Z18
	120	Z19	Z20	Z21
1000	30	Z22	Z23	Z24
	60	Z25	Z26	Z27
	120	Z28	Z29	Z30

Solid residues obtained after the thermal processing at 900-1000^{0}C (Figure 5.) contain negligible CaS amounts. Calcium silicates (CaS_iO_4) are contained in solid residues after thermal processing at 1000^{0}C of SCWHS mixtures with 30-40% of limestone.

The quantitative oxidation of initial SCWHS to Fe_2O_3 is observed after thermal processing at 1000^{0}C during 1-2 hours and intermediary products are Fe_xS_{1-x}.

So compositions of solid residues estimated with the thermodynamic simulation and obtained experimentally are nearly the same if the thermal processing is conducted during > 1hour at temperatures > 800^{0}C.

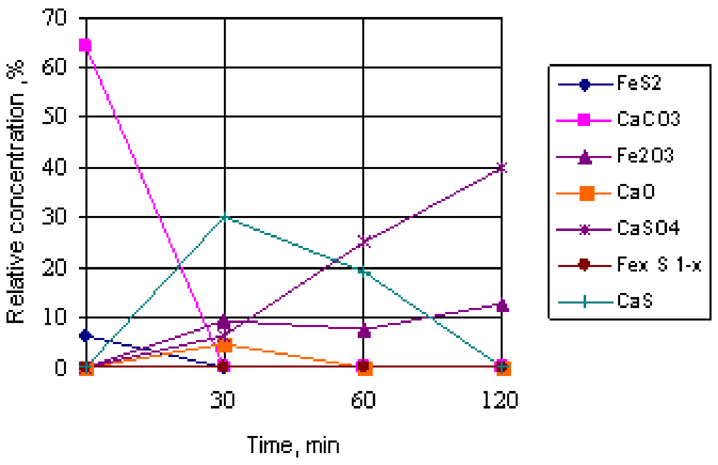

Fig. 5. **The influence of (mixture Z1, T = 1000 C) time on relative concentrations of Ca compounds**

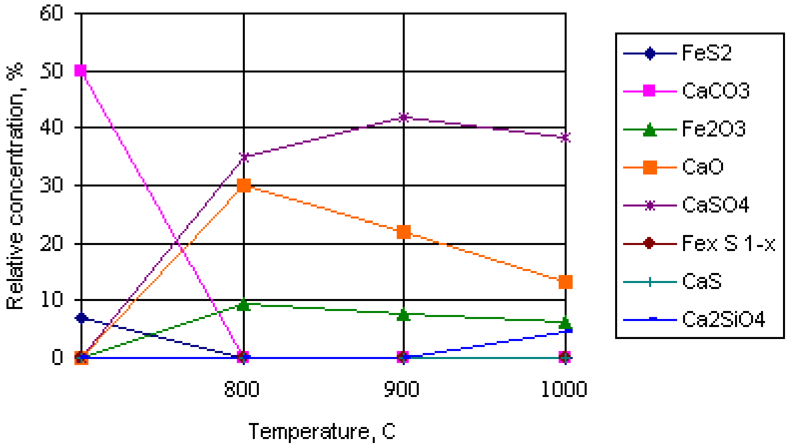

Fig. 6. **The influence of temperature on relative concentrations of Ca and Fe compounds after thermal processing of Z3 mixture during 120 min**

The increasing of carbon contents in initial SCWHS favor the thermal processing of limestone mixtures. However the growth of sulfur contents in initial SSCW impairs economical results of this process as $CaSO_4$ formed at temperatures 900-1000^{0}C has not binding properties and it is needed more quantities of limestone to obtain Ca $_2SiO_4$ having binding properties. So SCWHS with $S^d_t > 2\%$ and $C^d_t > 12\%$ are promising as a raw for this process probably.

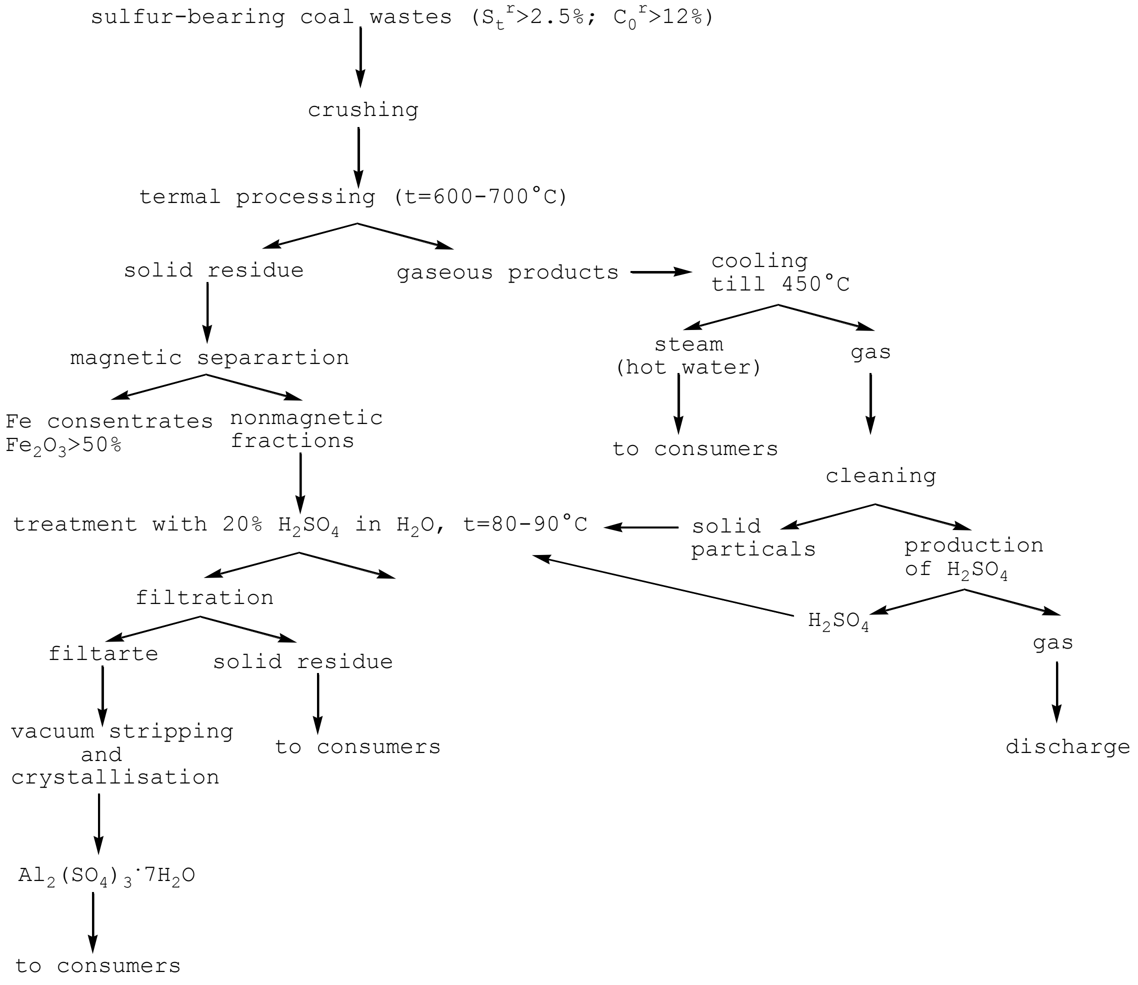

Fig. 7. **The principal stages of the processing of coal wastes with high kaolin contents**

The principal flow diagram of process of thermal processing of SSCW mixed with limestone presented in Figure 8.

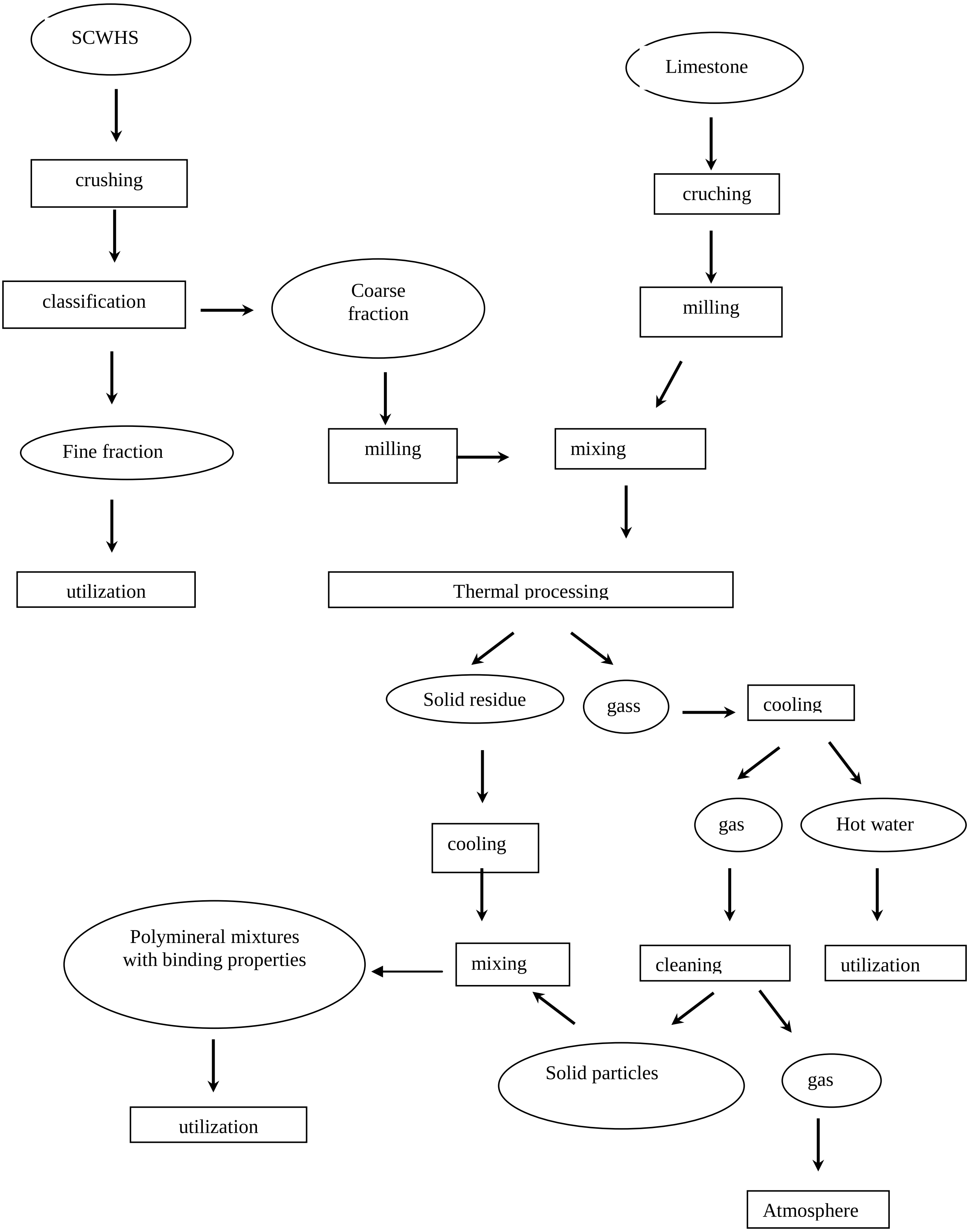

Fig. 8. **The principal technological process for the thermal processing of SCWHS mixed with limestone**

Conclusions

The following conclusions are based on the data of this report:

1. Storing of solid sulfur-organic bearing wastes ($S^r_t > 2.5\%$) in dumps is accompanied with dangerous actions on the environment due to the sulfides and organic substances oxidation. Two methods of thermal treatment of such wastes (SCWHS) are worked out to utilize them.
2. Sulfur bearing coal wastes (SCWHS) may be used to produce sulfuric acid along with some valuable products while sinterng in an oxidizing media at 650-750 ^{0}C or sulfur may be bound into the chemically stable substance ($CaSO_4$) while sinterng in an oxidizing media at 900-1000^{0}C mixtures of SCWHS and limestone in appropriate proportions. Solid residuals obtained by latter thermal processing are ecologically safe polymineral mixtures and can be used as a raw for producing local building material.
3. Sulfuric acid (91-93%)obtained using the commercial technique applied in situ with the thermal processing of SCWHS without additives may be applied to produce from solid residues aluminum sulfate and raw for building materials (bricks, porous aggregates for light concretes and other). The preliminary magnetic separation of above mentioned solid residues may produce a magnetic fraction which is an iron concentrate (> 50% of Fe) and a non-magnetic fraction which is a raw material for producing aluminum sulfate or an additive (up to 10%) to cement clinker or (after being ground) to cement , raw for obtaining above mentioned building materials.

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