ENVIRONMENT PROTECTION

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COMPLEX USAGE OF CLAY USED MATERIALS

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Abstract. *The article represents the results of research on the application of technological wastes of aerosol gas dynamic suspension treatment of aircraft elements for the heavy metal ions sorption from industrial wastewaters. The recommendations on utilization of polluted sorbents by depositing in constructional materials are represented.*

Keywords: clay; sorption; utilization wastes.

1. Introduction

Application of natural materials in technological processes greatly increases the overall ecological safety of production. For example, the usage of natural clay materials in processes of details recovering is very popular. But at the same time significant amount of waste material of given type is produced in result of the technological process of gas dynamic suspension aerosol cleaning of surfaces from contamination it is produced. Usually wastes from cleaning of details surface are utilized as sludge.

It is known that clay materials have good sorption properties regarding metal ions, but after sorption significant amount of wastes is created. Problem of waste sorbents accumulation is partially solved by the means of renewal of their sorption properties for the secondary usage in treatment technological processes. Nevertheless, the price of natural dispersion sorbents is not high; therefore their regeneration is not efficient. One of the prospective ways for utilization of waste sorbents is their application in construction as concrete filler.

Thus, there is possibility of complex usage of aerosol cleaning wastes as sorbents of metal ions and then as concrete fillers.

2. The problem statement

During the latest decade the processes of pneumatic and hydro-abrasive processing of details has changed towards improving their environmental features by replacement of working materials with soda, chalk, clay and fractional stone.

The consumption of working materials during processing depends on the type of surface pollution and speed of processing. But in any case it forms fine material waste with minor concentration of pollutants, which are not suitable for reuse [1].

The method of aerosol gas dynamic suspension cleaning of details surfaces from oil and coke deposits requires dark-brown loam (quarry Royische) as a working material. Typical consumption of solid fraction is 32 kg of loam per one nozzle apparatus per one working shift (8 hours). Thus, 8032 kg of used clay material are accumulated at the enterprise during a year (251 work days).

Usually waste from details metal surface processing by the aerosol gas dynamic suspension method are utilized as sludge. The wasted working suspension might be used for purification of runoff waters formed at enterprises. High adsorptive and ion exchange properties of clay materials make them efficient sorbents of heavy metals, petroleum products and surfactants.

Adsorption properties of sorbents depend on pores structure, size, and origin. The activity of sorbents is characterized with the amount of consumed pollutants per unit of their volume or mass (kg/m^3) [2].

Clay materials are characterized with good sorption properties regarding metals ions.

According to the investigation results [3] dark-brown loam absorbs Nickel ions and does not absorb Chromium ions. So, to provide increased sorption properties it is necessary to modify this loam.

The analyses of different methods of processing has showed that the most prospective way of modification of natural sorbents is their activation with chemical reagents (with the help of reagents it is possible to change chemical composition of sorbents for modeling of their properties) [4].

The essence of the method of acidic modification of natural mineral sorbents is in treatment of low active samples with solutions of sulfuric, hydrochloric, phosphoric and acetic acids during certain time intervals with heating and mixing. This method of influence on natural mineral sorbents, in fact, accelerates the processes that take place under natural conditions and influence of air, contentious pressure (process of chemical weathering in the zone of hypergenesis) and water with carbonic acid.

During acidic modification of natural mineral sorbents the following factors play an important role: nature of acid, mineralogical content of sorbent, quantitative ratio of acid and sample, degree of crystallization clay minerals, contained in natural sorbent, temperature of treatment and duration of activation.

The acidic activation of dark-brown loam in industrial conditions is the most efficient with application of sulfuric acid.

The process of activation changes the structure of natural loam: partial destruction of lattice takes place; active surface of clay is increased; sizes of clay particles are decreased due to their destruction; leaching of sesquioxides (like $A1_2O_3$) leads to formation of cavities; transformation of aluminosilicate silica particles in silica gel is observed; the porous structure of sorbents is changed (the diameter and pores volume increase).

3. The results of experimental investigations

Dark-brown loam was purified from impurities (mechanical impurities, sand) and grinded up. Then sulfuric acid was added in various concentrations (1%, 5%,10%,15%, 20%, 30%) to form of liquid suspension and 1 hour. Then clay was cleaned with distilled water in proportion 1:10 and settled. Created sediment was collected and dried under the temperature 105°C. Modified clay was weighted on analytical scales of the second class of accuracy (20 g/l of sewages).

To check the efficiency of dark-brown clay (quarry Royische) use as a natural sorbent for purification of Cr-containing sewages the experimental researches were conducted.

The dark-brown loam, modified with sulfuric acid in concentrations: 1%, 5%, 10%, 15%, 20%, 30%, was added (20g) in the given modeling solution of chromium ions with mass concentration of Chromium (III) 0,1 mg/l with volume 1 dm^3. The sample was taken every 5 minutes during half of hour. Measurement of Chromium concentration was conducted according to "The methodology of measuring Chromium concentration by photocomlimetric method" with photoelectric colorimeter KFK-3 in concentration range from 0, 01 to 0,2 mg/l, with total error (±δ) % of no more than 23%.

The figure 1 describes general dependence of Chromium ions sorption with dark-brown loam (quarry Royische) in time depending on modification. Modification of investigated sorbent with 10% solution of H_2SO_4 leads to the highest efficiency purification from Chromium ions. Changing of this variant of modification does not lead to significant purification effect. So, as a result of experiment it was proved that dark-brown loam modified with 10% solution of H_2SO_4 during 25 minutes decreases the concentration of Chromium ions (III) from 0,1 mg/l to 0,0027 mg/l. After half of hour the sorption process has decelerated and reduction of Chromium ions concentration has not been observed.

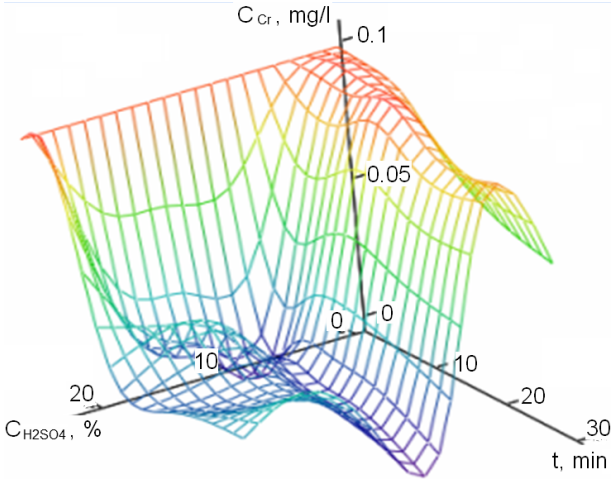

Fig. 1. Change of concentration (C_{Cr}, mg/l) of ions Cr (III) in modeling solution with time (t, min) depending on modification variant with sulfuric acid (C_{H2SO4}, %).

The final Chromium concentration has decreased in 37 times as compared with initial concentration. The purification efficiency is 97%, that states about efficiency acid modified dark-brown loam (quarry Royische) application as a sorbent for purification of sewage waters polluted with Chromium ions (III) (fig.2).

In result of runoff water sorption purification from Chromium ions by dark-brown loam

significant amount of sedimentation (2000 kg or 1 m^3 per 100 m^3 of runoff water) is formed. Formed sludge during purification of runoff waters of galvanic enterprise is industrial waste of IV hazard. It is one of the main polluters of environment with heavy metals.

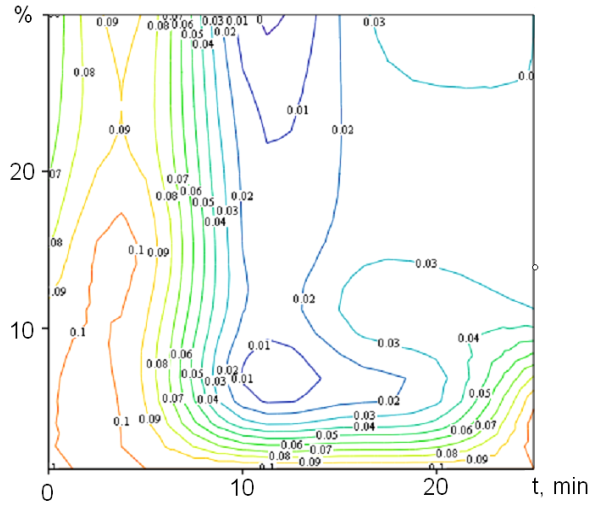

Fig. 2. Field of ions Cr(III) concentration depending on modification (%) variant and time (*t*) of investigation

The strategy for utilization of wasted sorbents from purification of runoff water from heavy metals is application of these sorbents in construction. Used sorbents might be used as efficient additives to constructional mixtures, if it is preserved strength parameters and there is not desorption [5].

As the, content of constructional mixture must meet the requirements of DSTU B.V 2.7-215 «Concretes. Rules for content selection». The study produced sediments grading was conducted by the method after Kachynsky (table 1). The data of calculation shows that dark-brown loam contains 25,75% clay, 58,39% sand, 15,86% rough dust, 21,73% dust and 4,02% slit. By the content of physical clay (25,75%) this sorbent belongs to light loams. Among fractions the predominant part belongs to sand (58,39%) and dust (21,73%). By grading after Kachynsky classification the given sample belong to light-loam sandy-dust. So, the wasted sorbent might substitute dust component in constructional mixtures according to DSTU B V 2.7-215.

Table 1. Granulometric content by dark-brown loam

Size of fractions, mm	Dark-brown loam	
	Content of fractions, %	Name by granulometric content
1 - 0,25	2,28	Light-loam Sandy-dust
0,25 - 0,05	56,11	
0,05 - 0,01	15,86	
0,01 - 0,005	12,36	
0,005 - 0,001	9,37	
< 0,001	4,02	
< 0,01	25,75	

The data of calculation shows that dark-brown loam contains 25,75% clay, 58,39% sand, 15,86% rough dust, 21,73% dust and 4,02% slit. By the content of physical clay (25,75%) this sorbent belongs to light loams. Among fractions the predominant part belongs to sand (58,39%) and dust (21,73%). By grading after Kachynsky classification the given sample belong to light-loam sandy-dust. So, the wasted sorbent might substitute dust component in constructional mixtures according to DSTU B V 2.7-215.

The possibility of used sorbent application in constructional mixtures is estimated based on desorption degree.

To define the efficiency of utilization of Chromium and Nickel containing wastes from runoff water purification experimental investigations on desorption were conducted (table. 2). According to DSTU B V 2.7-215 the filler in the quantity 5% was substituted with used sorbent (after purification of Chromium an d Nickel containing runoff waters of galvanic workshop of enterprise «Plant 410 CA»).

The analysis of experimental results proves that addition of used sorbent to constructional mixture does not lead to desorption of deposited ions of Chromium and Nickel. So, application of wasted sorbent as filler for constructional mixtures is possible [6].

Table 2. Desorption of Chromium and Nickel from constructional mixture

№ of sample	Place of sample taking	Sample characteristic	Concentration of Chromium and Nickel in distilled water after desorption, mg/l
1	Nickelling line, vessel of 1-st ablution	Cement + sand + dark-brown loam (5%)	≤ 0,02
2		Cement + sand + activated dark-brown loam 10% H_2SO_4 (5%)	≤ 0,02
3	Nickelling line, vessel of 2-nd ablution	Cement + sand + dark-brown loam (5%)	≤ 0,02
4		Cement + sand + activated dark-brown loam 10% H_2SO_4 (5%)	≤ 0,02
5	Chroming line	Cement + sand + activated dark-brown loam 10% H_2SO_4 (5%)	≤ 0,02

To evaluate economic efficiency of used sorbent utilization the comparative analysis of economic investments in technological process of purification of runoff waters from Ch (III) ions by the method of lime neutralization and sorption by investigated sorbent was performed. The consumption in both cases was defined per 100 m^3 of runoff water with the same concentration of Cr (III) ions (table 3).

Table 3. Comparison of different utilization methods of wasted materials

Utilization by standard method of neutralization	Utilization by proposed method – sorption
Consumption for purification of runoff waters (100 m^3)	
120 kg of lime 236 UAH	Wasted from cleaning of details 2000 kg 0 UAH
0 UAH	10% - 249 liters) 764 UAH
Expenditures for burial	
125 kg sludge 840 UAH	0 UAH
Total expenditures	
1076 UAH	764 UAH

The neutralization variant does not have expenditures for modification; sorption variant does not have expenditures for burial, because wasted sorbent is then applied in constructional mixtures. It may be profitable for enterprises due to reduction of expenditures for sand (50 UAH /t).

In result of analysis it was defined that economical effect from usage of clay materials is 312 UAH per 100 m^3 of runoff waters.

4. Conclusion

So, the study has proved possibility of complex usage of aerosol treatment waste on the example of dark-brown loam as a sorbent of Cr (III) ions and fillers for constructional mixtures. Nevertheless, the application of clay material in comparison with neutralization method gives economic profit of 312 UAH.

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О.Л. Матвєєва[1], Є.О. Бовсуновський[2], О.В. Лапань[3], О.В. Рябчевський[4]. Комплексне використання відпрацьованих глинистих матеріалів

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Розглянуто деякі аспекти використання мінеральних відходів промислового виробництва у очищенні стічних вод, що утворюються на об'єктах машинобудування, у тому числі авіаційної галузі. Представлено результати очищення промивних стічних вод гальванічного виробництва за допомогою мінеральних сорбентів від іонів нікелю та хрому. Надано рекомендації щодо наступної утилізації відпрацьованих сорбентів з метою зменшення ризику вторинного забруднення навколишнього середовища.

Ключові слова: відходи; глина; сорбція; утилізація.

Е.Л. Матвеева[1], Е.О. Бовсуновский[2], О.В. Лапань[3], О.В. Рябчевский[4]. Комплексное использование отработанных глинистых материалов

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Рассмотрены некоторые аспекты использования минеральных отходов промышленного производства в очистке сточных вод, которые образуются на объектах машиностроения, в том числе авиационной отрасли. Представлены результаты очистки промывочных сточных вод гальванического производства с помощью минеральных сорбентов от ионов никеля и хрома. Даны рекомендации относительно утилизации отработанных сорбентов с целью уменьшения риска вторичного загрязнения окружающей среды.

Ключевые слова: глина; отходы; сорбция; утилизация.

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