International Journal of Engineering & Technology, 7 (2.23) (2018) 38-41

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Research of the opportunity to use sludge wastes of ferrovanadium production as pigments for silicate paints

Starostina I.V.[1]*, Kosukhin M.M.[1], Simonov M.M.[1], Starostina Yu.L.[1]

[1]FSBEI HPE «Belgorod State Technological University named after V.G. Shukhov», Belgorod, Russia (308012, Belgorod, Kostyukov str. 46).
**Email: starostinairinav@yandex.ru*

Abstract

The article considers the urgent problem of formation, storage and recycling of sludge materials of various compositions, generated as a result of industrial enterprises wastewater treatment and sanitation. It is pointed out that in spite of a lot of designs concerning the wastewater neutralization sludges recycling, the share of their efficient usage is still negligible. So, one of the most relevant trends of nature protection activity and the rational use of natural resources is developing a technology of these wastes reclamation and applying them for useful products manufacturing. The research of chemical, mineral and grain composition of ferrovanadium production sludge wastes, generated at waste waters neutralization at the «EVRAZ Vanadii Tula», Tula, Russia, has been carried out. A method of obtaining pigments for silicate paints on the basis of these sludges has been considered. The influence of the sludges' thermal treatment conditions on their mineral composition and the properties of paints based on them has been evaluated. The pigments content varies from 1 to 3 %. It has been demonstrated that the most promising is the usage of initial sludges and heat-treated at temperature 1000°C sludges as pigments for high-performance silicate paints.

Keywords: *Sludges, liquid glass, pigment, covering capacity, low-basic hydrated calcium silicates.*

1. Introduction

Under the modern conditions of industrial production development intensification one of the most essential problem is the protection of environment against polluting it with hazardous substances. Over 800 mln tons of sludge materials of various composition and properties are generated in Russia every year, which are virtually not recycled and are accumulated at dumping places. The sludge sediments are formed as a result of sanitation and neutralization of acid industrial wastewaters from the enterprises of nuclear power engineering, machine-building, electrical engineering industry, chemical and pharmaceutical industry and other branches. As a neutralizing agent most often the lime-containing materials are used, which determines the chemical and mineral composition of the generated sludges.

The structure of sediment, formed in a supersaturated solution depends on the ratio of molecular aggregation and molecular orientation velocities, so it can be amorphous, crystalline or mixed. They are characterized with the variability of chemical and mineral compositions, high water-retention capacity, and the substantial content of heavy metals ions, which preconditions their high toxic, carcinogenic and mutagenic effects on living organisms. These characteristics explain the low level of these materials reclamation, which has categorized them as nonutilizable waste. By their environmental impact degree galvanic sludges take one of the first places among industrial wastes [1].

The processing of such sludge products is burdensome for enterprises, so after the neutralization these wastes are dumped to sludge reservoirs for dehydration and long-term storage. But it doesn't solve the problem of environment protection, as even after the neutralization, contained in water in form of slightly-soluble compounds, the sludges remain toxic to this or that extent. Besides, in the process of constant dumping of waterlogged waste into the sludge reservoir a free filtration flow, typical for such wastewater facility, is formed, which has adverse effect on both its foundation and the environment [2]. This can result in flooding of certain elements of sludge reservoir (embankments) and in the draining system disfunction, which can cause the accidental spills of millions of cubic meters of sludge wastes to the surrounding territory and the nearby water bodies [3].

When the sludges are dried, a dusty cloud can be formed, which after settling can pollute water bodies and soils, and can cause the migration of substances, contained in the dust. Thus, from 1 ha of dry surface of a sludge depository about 2-5 tons of fine dust a day [4] can be blown away. As a result, the increased amounts of metals, such as zinc, copper, manganese, chromium, lead, iron etc., get to the soil around the sludge depository.

At the same time, when there is no safe shielding of the sludge reservoir foundation the filtration flow can penetrate into the foundation and then into the underground waters of the surrounding area, which results in hydrochemical pollution of underground waters [5]. The penetration of heavy metals ions to soil and water causes the anthropogenic geochemical anomalies in atmosphere and hydrosphere, can impede the life activity of soil bacteria, which determine the soil fertility. So, the currently used technologies of sludge wastes long-term storage imply the permanent allocation of large areas for their pollution without the opportunity of their further utilization.

The conditions of long-term storage at dumping sites and sludge depositories also affect the properties of sludge materials themselves. Thus, some mineral sludges can coagulate and partially self-cure due to crystallization processes. This can result not only in the alteration of mineral composition, but also of a number of physical and chemical characteristics - chemical reactivity and dispersity, which deteriorates the consumer properties of the sludges.

Nowadays the application of sludge wastes of various compositions as secondary raw materials or admixtures, which allow improving the quality and cut production costs of the final products, is a promising and efficient way of their recycling.

The most large-capacity sphere of using sludges, containing heavy metals, is building materials production [6], especially the production of ceramic materials - bricks [7, 8] and expanded clay gravel [9, 10]. This is due to the fact that ceramics production implies high-temperature processes, which bind the heavy metal ions by their sintering with silicate или aluminum silicate materials, with the subsequent formation of unleachable forms, which prevents their migration into the environment even at the most harsh operating conditions of the obtained products [11].

There can be also other ways of sludge materials reclamation. In work [2] the opportunity of using the sludge from heat and power facilities, formed in water-treatment system at water clarification stage, as filler for gypsum binders, is described. The sludge content in amount up to 10% doesn't reduce the strength characteristics of the obtained gypsum composites.

The integrated processing of galvanic sludges has been researched [12]. At the first stage the heavy metals in the form of hydroxides – $Fe(OH)_2$, $Ni(OH)_2$ and $Zn(OH)_2$ – are selectively separated by means of acid-alkali treatment, which can be used in production of loading pigments, enamels, polyoxide catalysts. The gradual extraction of heavy metal ions reduces their content in the treated sludge, which allows reducing the hazard class of galvanic sludge to 4 and 5, and using them in building materials and roadway covering production etc.

There are suggestions to use the metallurgical sludge, which contains iron, zinc, nickel and chromium ions, as a fertilizer for flax growing [13]. Thus, the results of biochemical studies have shown that in small concentrations heavy metals can optimize metabolic processes in the plant cells of flax.

The article [14] considers the usage of galvanic sludge at obtaining magnetic sorbents for oil-containing wastewater purification.

But it must be mentioned that heavy metals, contained in sludge wastes, possess chromophoric properties and can be considered as secondary raw stuff for industrial pigments production.

The synthesis of mineral pigments is based on high-temperature processes, at which the solid-phase physical and chemical reactions take place, at which the nonsoluble spinels, silicates and other compounds are formed, which determine the color of the obtained pigments [15]. The silicatization of sludges binds the toxic compounds, and reduces the migration ability and toxic activity of heavy metals to the allowable values.

Though a lot of research has been carried out concerning the application of galvanic ferriferrous sludge wastes, the growing tendency of the sludge generation amounts and the fullness of the existing sludge depositories indicate the necessity to search new ways of their reclamation.

In the protective-decorative finishing technology of interior and external surfaces of buildings and constructions the silicate paints are widely used, based on liquid potassium and sodium silicate glasses (Na_2SiO_3) as a binder, carbonaceous fillers and various pigments. The purpose of this research work is studying the opportunity of using sludge wastes of vanadic pentoxide and ferrovanadium alloys production as pigments for silicate paints. To achieve the set purpose the following objectives were considered:

- determining the general properties of sludge wastes;
- the influence of thermal treatment conditions on the composition and properties of the used sludges;
- the influence of sludge wastes content in the raw charge on the basic physical and mechanical properties of the obtained silicate paints.

2. Material and Methods

As an object of research the sludge materials, generated at the neutralization of acid wastewaters from «EVRAZ Vanadii Tula» enterprise, Tula, Russia.

The mineral composition of sludges was researched by means of X-ray phase analysis with a diffractometer «DRON-2.0».

The sludges were prepared according to the following methodology. The initial sludge was dried at temperature 55°C to the residual moisture content 0.5 - 1%. The thermal modification of sludges was performed by heating the averaged samples with the access of oxygen in the electric furnace SNO 25/12 within the temperature range 600°C - 1100°C with the 1 hour exposure at the maximum temperature. The obtained products (initial and heat-treated) were then milled to the specific surface, characterized with the sieve 0056 residue not above 1%. As a binder the sodium water glass was used - silicate module 2.5; density 1.15 g/cm^3. As a filler – the finely-dispersed industrial chalk ($CaCO_3$).

3. Results and discussion

The sludge materials under consideration are sediment formed at the neutralization of industrial waters from vanadic pentoxide and ferrovanadium alloys production by hydrometallurgical method. The acid wastewaters generated in conditions of technological cycle are neutralized with lime through a two-stage cycle. It results in the formation of 2 types of wastes, notionally named ferriferrous concentrate (FFC) and limestone-gypseous composition (LGC).

The annual volume of sludges generation amounts to over 100 thousand tons. At present, due to lack of efficient recycling methods, the great bulk of these sludge wastes are virtually not recycled, but dumped at sludge depositories, which degree of fullness is already 95%. The chemical composition and some technological characteristics of materials under study are presented in Tab. 1, 2.

Table 1: The chemical composition of sludge materials, wt. %

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	Cr_2O_3	SO_3	Na_2O	TiO_2
FFC	16.68	11.01	2.20	32.48	0.88	4.38	3.00	19.11	0.23	6.83
LGC	37.14	2.22	0.32	0.71	4.04	17.67	0.06	33.11	0.20	–

Table 2: Some technological characteristics of FFC

№	Characteristics	FFC	LGC
1	Loose density, kg/m^3	1020 – 1100	640 – 700
2	True density, kg/m^3	2150 – 2200	1480 – 1530
3	Specific surface, cm^2/g	2200 – 2500	2800 – 3300
4	pH water extract	4.5 – 5.2	11.9 – 12.4
5	$CaSO_4{\cdot}2H_2O$ content, wt. %	20 – 29	65.0 – 90.0

Concerning their chemical and mineral composition LGC and FFC can be classified as polymineral materials [10], containing calcium sulphate and carbonate, ferriferous components - Fe_2O_3 and FeO, the sulphatic form of hydrated calcium sulfoferrite, metals hydroxides and the residual amount of lime (fig. 1). Besides, the LGC and FFC sludge materials include heavy metals, the content of which is presented in Tab. 3. The wastes under study belong to hazard class 4.

Table 3: The heavy metals content in sludge materials, mg/kg

Material	Cu	Zn	Cd	Pb	Co	Ni	Cr
FFC	3.25	26.8	0.027	3.88	0.84	3.34	6681.0
LGC	6.23	20.8	0.44	3.04	2.11	6.42	105.3

FFC is a black paste-like finely-dispersed mass with moisture content up to 25%. Its distinctive feature is the iron oxides content over 30%, and the presence of heavy metals – manganese, vanadium, chromium. According to the mineral composition evaluation (fig. 2), the high content of amorphous phase should be mentioned, presented mostly with metal hydroxides; the iron oxides – wustite, hematite, as well as calcium sulfate dihydrate and calcium carbonate [16] are recorded.

LGC is a dark brown sludge with moisture content over 50%. According to the X-ray phase analysis results (fig. 2), LGC is characterized with a high degree of crystallineness; among the minerals the predominant content of calcium sulfate dehydrate should be noted – up to 90%; the residual content of lime is recorded, which provides the alkaline medium of the material water extract (pH up to 14), and a certain quantity of ferriferous components – iron oxides and hydrated calcium sulfoferrite.

The initial and thermally treated LGC and FFC sludges were milled and used as pigments in the silicate paint. The content of initial and thermally treated sludges was altered from 1 to 3%. The physical and mechanical properties of the obtained silicate paints were determined – covering capacity, weather resistance, adhesion and impact strength.

The interaction mechanism of sodium silicate with initial and thermally modified sludges consists in the following: at the blending of liquid glass and sludge materials the free CaO is partially hydrated on the surface of sludge particles with the formation of $Ca(OH)_2$ and interacts with sodium silicate with the formation of low-basic hydrated calcium silicates –Ca–O–Si–O–H .

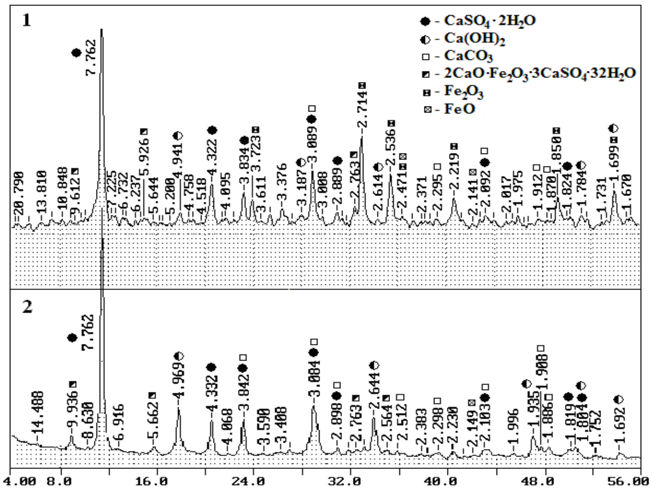

Fig. 1: The X-ray phase analysis results of ferrovanadium production sludges: 1 – FFC; 2 – LGC.

The calcium-hydrate, hydrate-silicate and carbonate compounds are formed, which are necessary for providing the silicate paint with high strength and other technological characteristics.

The findings of the research have shown that the increase of the treatment temperature from 600 to 900ºC results in the increase of the pH level of the pigments' water extracts (fig. 2) from 8 to 12 (for LGC) and from 6 to 7.89 (for FFC) due to the formation of free CaO as a result of the partial decomposition of sludge components - carbonate, sulphate and hydrated calcium sulfoferrite.

As the X-ray phase analysis results confirm – the intensity of the corresponding peaks is reduced (fig. 3), the amorphous background decreases, the maximum peaks intensity of CaO and dehydrated $CaSO_4$ (anhydrite) is increased. Then CaO is hydrated with the formation of $Ca(OH)_2$ and the intensive interaction with sodium silicate which forms low-basic hydrated calcium silicates.

The excess formation of $Ca(OH)_2$ creates the internal stresses and defects, which in the course of time results in crack formation, peeling of the paint coating and reduction of its weather resistance.

The increase of the sludges baking temperature to 1000ºC results in the formation of a properly sintered product, in which decomposition processes of carbonates, hydroxides, sulphates were complete enough, with the subsequent formation of new compounds, mostly of spinel structure and solid solutions.

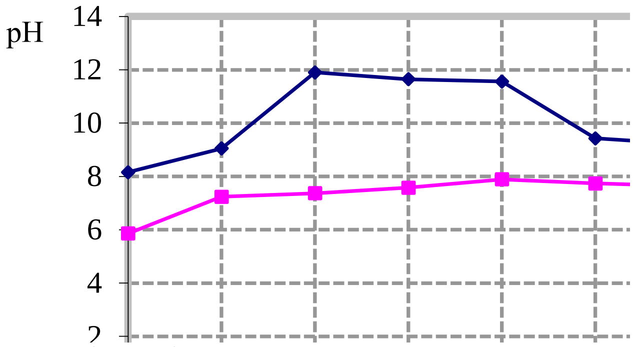

Fig. 2: The influence of LGC and FFC sludge materials baking temperature on the pH level of water extracts.

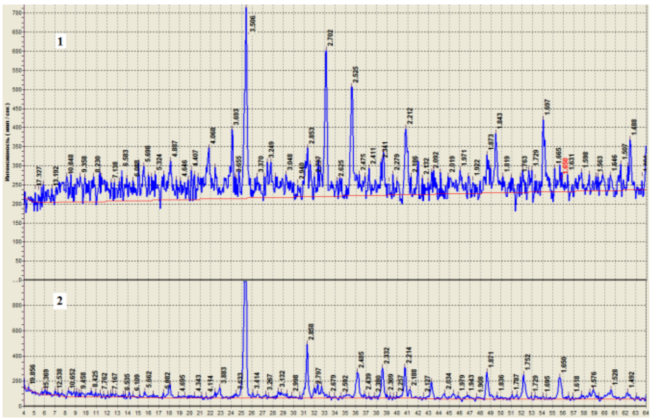

Fig. 3: The X-ray phase analysis results of ferrovanadium production sludges, treated at temperature 1000°C: 1 – FFC; 2 – LGC.

This has an effect on the pH level of water extracts – a certain lowering of pH level to 9.43 for LGC (fig. 3) is observed due to the involvement of the free CaO, formed as a result of the LGC components decomposition, into the processes of sintering and partial vitrification.

The residual amount of CaO is intensively hydrated with the formation of $Ca(OH)_2$, and also interacts with the liquid glass (Na_2SiO_3), forming the low-basic hydrated calcium silicates. At this, silicate paints are characterized with the increased weather resistance – there are no cracks or damage of the coating integrity.

The increase of LGC and FFC baking temperature to 1100ºC results in the strong sintering of products to their vitrification, which is accompanied with the subsequent, though slight, absorption of CaO and, consequently, the decrease of the pH level of the obtained pigments water extracts – for LGC up to 9.2 , for FFC up to 7.64 (fig. 2).

In general, a trend to the color lightening with the increase of the pigments synthesis temperature over 1000ºC is observed: for LGC the pinkish tones appear, and for FFC the light-grey tones. The hard sinters, obtained as a result of LGC baking at temperature 1100ºC, require the longer milling time, which increases energy consumption for obtaining the final product and makes it difficult to obtain the material of the required dispersity. The high dispersity of a pigment is one of the most essential characteristics, as it has influence on the color properties of the obtained paint – color strength and intensity, and contributes to the increase of the pigment's reaction capacity at the interaction with the paint binder, in this case – with liquid glass. All this together has a significant effect on the quality of the obtained silicate coating. Therefore, as the optimal conditions of the studied sludges' heat treatment, with the purpose of obtaining pigments for silicate paints with advanced properties, the temperature of 1000ºC is recommended.

In Tab. 4 and 5 the compositions and technological characteristics of silicate paints with LGC and FFC sludge materials used as pigments, both initial and heat-treated at temperature 1000ºC. The thermal treatment of sludges contributes to the reduction of the paint's covering capacity while preserving the other properties at the high level.

Table 4: Compositions and properties of silicate paints with FFC sludges used as pigments

Components and indices	Composition						
	con-trol	Initial FFC			FFC thermally treated at 1000°C		
Liquid glass	50	50	50	50	50	50	50
Chalk, %	50	49	48	47	49	48	47
Pigment (sludge), %	0	1	2	3	1	2	3
Covering capacity , g/m^2	461	378	376	345	283	231	203
Adhesion, points	2	2	2	1	2	1	1
Weather resistance	No cracks and flaking						
Impact strength, kg/cm^2	50	50	48	45	47	45	45

Table 5: Compositions and properties of silicate paints with LGC sludges used as pigments

Components and indices	Composition						
	con trol	Initial LGC			LGC thermally treated at 1000°C		
Liquid glass	50	50	50	50	50	50	50
Chalk, %	50	49	48	47	49	48	47
Pigment (sludge), %	0	1	2	3	1	2	3
Covering capacity , g/m^2	461	341	335	329	277	261	225
Adhesion, points	2	2	1	1	2	1	1
Weather resistance	No cracks and flaking						
Impact strength, kg/cm^2	50	45	45	45	45	45	45

It must be pointed out that silicate paints, obtained by using pigments based on initial sludges and the sludges, thermally treated at 1000ºC, have the universal adhesion to silicate surfaces – concretes, mortars, bricks and have high impact strength.

4. Conclusion

The sludge wastes, formed at the neutralization of industrial waters from vanadic pentoxide and ferrovanadium alloys production with hydrometallurgical method, can be used as pigments for obtaining silicate paints for external and interior surfaces of buildings.
The most promising is the usage of initial sludges and the sludges, thermally treated at temperature 1000ºC. The obtained LGC-based pigments are brown, and the FFC-based pigments are grey-black. The silicate paints produced with the use of the designed pigments in amount of 1-3 wt.% have the increased weather resistance and high impact strength, as well as the universal adhesion to silicate surfaces – concretes, mortars and bricks. The application of thermally treated pigments allows reducing the covering capacity of silicate paints.

Acknowledgement

The work is realized in the framework of the Program of flagship university development on the base of the Belgorod State Technological University named after V.G. Shoukhov, using equipment of High Technology Center at BSTU named after V.G. Shoukhov.

References

[1] Verbol S.V., Zapary M.M., Kozlov V.V., "Neutralization of galvanic sludges with the extraction of metals", *Ecology and industry in Russia*, No. 4, (2000), pp. 20 – 29.
[2] Valeev R.Sh., Shaikhiev I.G., "Recycling of sludge wastes from heat and power facilities in building materials production", *Ecology and industry in Russia*, No. 2, (2010), pp. 28-29.
[3] Korneev V.I., Suss A.G., Tsekhovoy A.I., *Red sludge - properties, storage, application*, Moscow, Metallurgy, (1991), p. 144.
[4] Kichigin E.V., Yastrebinsky R.N., Tikunova I.V., "Binding stabilization of dust surfaces of tailings pond beaches", *Journal of Mining*, No. 2, (2009), pp. 72-74.
[5] Valeev R.Sh., Shaykhiev I.G., "Recycling of sludge wastes from heat and power facilities in building materials production", *Industrial ecology and safety: proceedings of the 3rd scientific conference*, (2008), pp. 24-26.
[6] Vasilenko T.A., "Use of mineral sludge in the production of building materials", *Modern problems of science and education*, No. 5, (2013), available online: www.science-education.ru/111-10032
[7] Fomina O.A., Stolboushkin A.Yu., "Formation of the rational porous structure of walling ceramics of iron-ore sludge waste", *Building materials*, No. 12, (2015), pp. 14-19.
[8] Sapronova Zh.A., Sapronov D.V., Starostina Yu.L., "Combined extender pigments based on industrial wastes", *Solid State Phenomena*, No. 265, (2017), pp. 450-455.
[9] Levitsky I.A., Pavlyukevich Yu.G., Bogdan E.O., Kichkailo O.V., "The expanded clay gravel production with the use of galvanic wastewater sediment", *Glass and ceramics*, No. 7, (2013), pp. 23-27.
[10] Starostina I.V., Simonov M.M., Denisova L.V., "The use of ferrovanadium production sludge wastes in claydite gravel technology", *Solid State Phenomena*, No.265, (2017), pp. 501-506.
[11] Abdrakhimova E.S., Abdrakhimov V.Z., "The direction and sequence of reactions, proceeding at baking clay minerals with the increased iron oxide content", *Bashkiria chemical journal*, Vol.13, No.2, (2006), pp. 54-55.
[12] Olshanskaya L.N., Lazareva E.N., Egorov V.V., Sorokin A.A., "The application of electroplating industry sludge for consumer goods production", *Polzunovsky vestnik*, Vol.4, No.2, (2011), pp. 203-205.
[13] Shubina A.G., Sinyutina S.E., Gusev A.A., Shubin R.A., Abramova S.V., "On the question of using the recylced metallurgical sludge as a fertilizer", *Bulletin of TSTU*, Vol. 21, No. 3, (2015), pp. 470-474.
[14] Dolbnya I.V., Tatarintseva E.A., Shaykhiev I.G., Kozmich K.V., Komissarenko M.V., "Purification of oil-containing wastewaters with magnetic sorbents based on the ferritized galvanic sludge", *Bulletin of Technological University*,Vol.19, No.23, (2016), pp. 154-156.
[15] Zainullin Kh.N., Babkov V.V., Zakirov D.M., Chulkov A.N., Iksakova E.M., *Utilization of deposits of wastewater of galvanic productions*, Moscow: "Ore and metals" publishing house, (2003), p. 272.
[16] Starostina I.V., Pendyurin E.A., Tolitchenko A.V., "Research of physical and chemical properties of ferrovanadium production sludge wastes", Bulletin of BSTU named after V.G.Shukhov, No. 1, (2013), pp. 129-132.