

**RECOVERY OF TECHNOGENOUS WASTES IN THE PRODUCTION
OF PIGMENTS AND FILLERS**

L. G. Gerasimova, M. V. Maslova

Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Resources,
Kola Scientific Center, Russian Academy of Sciences, Apatity, Murmansk oblast, Russia

Abstract

The issues of solid waste enrichment disposal and processing of mineral raw materials, ash from burning of liquid and solid fuels and waste chemicals are relevant worldwide. The growing volume of the production and processing of raw materials increases the amount of waste, creating environmental problems which are particularly serious for northern regions. This makes the current research on recycling with the production of new products relevant and pressing; there is a great demand at present for these products on the Russian market. Industries that use large amount of raw materials include the construction and paint industries. Specifically, in these industries pigments and fillers are widely used. In the domestic market, these materials are in short supply, which limits their wider use.

1. INTRODUCTION

Since nowadays natural resources for the production of pigments and fillers are either running out or require sizable capital investment, it is important to involve into industrial processing the mineral wastes of operating enterprises.

The purpose of research and implementation in this area (Nikolaev, 1991; Fedorov, et al., 2003) has been manifold: to integrate the approach to resource processing by diminishing the volume of waste, to intensify the effectiveness of resources utilization, tackling at the same time some social issues in the regions, in particular, creating new jobs and replenishing the local budgets. It is obvious that, in order to appreciably diminish the amount of current wastes, the market for the new products should have a substantial capacity. There are, indeed, industries operating with bulky material flows, namely, construction and production of paint and lacquer with an ever growing demand for pigments, pigment fillers, dispersing compounds, and thickening materials. Products with pigment properties are also indispensable in plastic, paper and rubber manufacture. In Russia, both their production and utilization are fairly limited. As the result, the annual per capita consumption of paint and lacquer materials here is 3-4 kg, whereas in Europe and USA it is 15-18 kg (Gerasimova, 2001; Gerasimova and Nikolaev, 1999).

In the potential developments, of special interest are composite pigments containing titanium, iron, aluminium, silicium, and calcium compounds in different combinations (Goldberg, 1976; Larionov and Zorin, 2003). As a rule, the properties of an entire composite are determined by the pigment component covering the core surface represented by known synthetic and natural fillers such as calcite, alumina, silica, talc. Products with these composites take on pigmenting or filling properties. The former is tinturing products and making them more attractive, the latter- improving their technical characteristics such as stability to heat, light and aggressive media, increased impact and bending strengths, etc. Mineral composites can be produced from polycomponent mineral wastes of ore mining and dressing enterprises (Kuleshova, 2002).

Recovery of copper-nickel ore dressing wastes

Copper-nickel dressing tailing dumps (the Kola MMC) contain high contents of layered silicates which can be processed to obtain effective fillers (Makarov V.N., et al., 2001). In this study, products dumped after magnetite removal were used. The mineral composition, w/o, is given in table 1

Table 1. Mineral composition of products dumped after magnetite removal, mass. %

Talc	87.53	Olivine	-
Magnetite	0.62	Serpentine	2.04
Carbonate	2.16	Quartz	1.12
Amphibole	6.03	Biotite	0.49

The finely ground undoped samples are light-grey (unheated) or light-brown (after calcination at 850°C). Their whiteness index is not higher than 64%. However, if mixed with an organic binder, the product easily covers the surface and can be classed among pigment fillers (Fedorov, et al., 2003). When the fine fraction (< 28 µm) of the light-grey product was used as a core of the coloured pigment shell, we obtained coloured pigment fillers in both liquid and solid-phase regimes. Intense and uniform colour tones are achieved due to laminated core structure and its high specific surface area (Kochergin and Krasnobay, 2003).

Although the wastes contain an oxidizing copper-nickel sulphide impurity, it does not affect the quality of the target product. Moreover, it enhances its brightness and resistance to weather impact (such as light, water, etc.). Table 2 presents the synthesis parameters and main properties of the pigment filler. It can be used in the production of coloured compositions with satisfactory properties. Pre-treatment (mechanical activation) and coating by a flatted agent (Fe, Ni, Co, etc), improves its quality and expands its scope of use.

Table 2. Manufacturing conditions and properties of pigment fillers

№	Manufacturing conditions		pH of aqueous extract	WSS, %	HP g/cm ²	Colour
	Addition to the initial sample, %	Heat treatment, °C				
1	-	-	7.32	2.56	295.3 (glazes)	Light-grey Light-brown
2	-	150	6.60	0.56	250	
3	-	850	7.25	0.28	113	
4	CoCl ₂ - 2.5%	900	7.37	0.3	84.5	Dark-grey Brown (bright) Reddish-brown
5	FeSO ₄ ·7H ₂ O - 10%	500	7.34	2.1	12.5	
6	-«-	850	7.46	1.4	17.5	
7	Fe ₂ NiO ₄ - 2.5%	-	7.20	0.5	20.2	Light-brown Brown
8	Fe ₂ NiO ₄ - 5%	-	7.31	0.35	27.7	

Note: SC means hiding property, g/m^2 ; WSS– water-soluble salts, %; Fe_2NiO_4 is dark-brown iron-nickel reject (“Severonikel”).

This work demonstrates the recovery potentials for some of the polymineral wastes in Russia in the production of filler materials for building purposes.

Obtaining pigments and fillers from coal-firing ash

The ash of thermal power plants is a bulky industrial waste. The environmental hazard in this case is the fine fractions of solid coal-firing waste. At the same time, this waste has a synthetic origin and can be turned into better fillers than those made from natural minerals, primarily because they are in a disintegrated state, which makes unnecessary, or sharply reduces, the energy expenditures on grinding.

The ash of the Apatity thermal power plant mainly contains the following elements (in terms of oxides), weight %: SiO_2 - 54-55, Al_2O_3 - 16-17, Fe_2O_3 - 15-17, MgO - 2.5-3.0, with trace amounts of Ca, Na, K, Ti, and other elements. The feed product (the pigment shell carrier) was the fine fraction ($<50\text{ }\mu\text{m}$) of entrained ash.

The prepared ash products were coated with hydrate oxides of some metals, such as Fe (III), Ti (IV) and others. After treatment, the product was calcined to obtain fillers or pigment compositions of a wide colour range. Such pigments are now regarded as good substitutes for monopigments in the paint-and-lacquer and plastic production (Gerasimova 2001) on account of their lower cost and higher product quality.

Unfortunately, it is very difficult to obtain good-quality pigments without any pre-treatment (Gerasimova, et al., 1998). There are two type of pre-activation for entrained ash: mechanical (grinding) and chemical (treatment in diluted acid solution). For chemical activation, the ash was treated with sulphuric and hydrochloric acids (50-100 g/l H_2SO_4 or HCl). The ash suspension was kept in acid solution (S:L = 1:3-5) for 3 hours under stirring and heating to 70°C . Then the liquid phase was separated, the precipitate washed on a filter with water (S:L = 1:3) and calcined at $700\text{--}800^\circ\text{C}$. The final product was disaggregated in a porcelain mortar to determine the main pigment characteristics: hiding property, aqueous extract pH, and the content of water-soluble salts. The determinations were carried out following the techniques set in the State Standard Specification 9808-84 (Gerasimova, 2001).

The new method for ash pigments production included acid treatment, washing of the solid and modifying of the ash particles surface, which either improved the painting characteristics (ZnSO_4 , $\text{Al}_2(\text{SO}_4)_3$, Na_2SiO_3) or intensified the filler colour (Fe, Co, Ni compounds). Lastly, the modified product is calcined at $250\text{--}850^\circ\text{C}$. On the run of pilot-scale test, beige and yellow-brownish products were synthesized from ash. The scheme of the beige product production is demonstrated in Fig.1. The pigment fillers have been tested at the “Spektr” scientific production association in Yaroslavl. It was found this pigment can be used as components of oil and enamel paints. Table 3 shows the test data of one of the products obtained following the scheme, namely, the yellow-brownish pigment filler. Some of the specific functions performed by the ash filler-based pigments include correcting of the rheological properties of the paint, increasing the pigment stability in stored PLM, and enhancing the weather resistance.

Chemical activation imparts a better quality to the finished iron-containing pigment; this includes higher organoleptic and hiding properties, and WSS contents. The colour of the pigment is brighter due to the action of sulphuric acid, cleansing the surface from iron compounds and smoothing over the rough areas via chemical interaction with aluminium and silicium compounds. Moreover, the degree of iron precipitation for the ash treated by sulphuric acid is higher (by about 10-13%) in comparison

with that observed in the experiments with the mechanically activated ash. The colour of the latter is dull and it doesn't cover the surface.

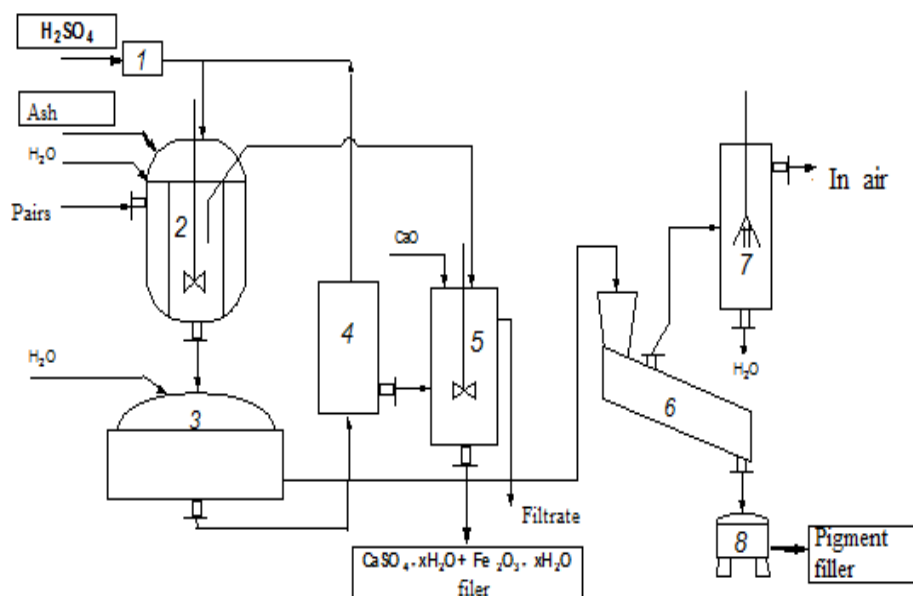


Fig.1. Principal apparatus-technological scheme of the beige filler

1-dispenser, 2-reactor with a jacket, 3-drum filter, 4-collector, 5-reactor, 6-furnace, 7-scrubber, 8-dismembrator.

Table 3. Production of ash-based iron-containing pigments *

Initial ash, g		Fraction, <63μm, %	Iron precipitation on ash, %	Pigment properties		
FeSO ₄ ·7H ₂ O	Fe-shavings			Hiding property g/m ²	Aqueous extract pH	WSS, %
Mechanical activation of initial ash						
5	3.0	95.1	85.3	21.4	7.4	0.80
10	1.6	98.0	80.1	20.1	7.0	0.68
30	1.6	93.2	35.0	20.3	6.8	0.91
10	1.6	98.0	98.0**	21.3	7.0	1.40

Chemical activation of initial ash						
5	3.0	95.0	98.0	15.4	7.0	0.42
10	1.6	95.0	92.1	12.8	7.1	0.51
30	1.6	95.0	42.1	18.1	7.4	0.80
10	1.6	95.0	98.0**	17.4	6.9	0.55

*) Experimental conditions: $P_{\text{ash}}=30$ g, $t=65-70^{\circ}\text{C}$, τ - 6 hours, $S:L=1:3$ ($t_{\text{calc}} - 850^{\circ}\text{C}$)

**) unwashed solid.

The quantity of “ash” pigments and fillers incorporated in enamel and oil paints was found to be varying between 13 and 42 weight % (Gerasimova, 2001). The scheme of pigment and filler manufacture has been successfully tested at a pilot plant of the Central Laboratory of Apatit JSC (Bolshakov, 1978). These products have a broad field of use and can be very attractive. New materials may expand the range of products and relieve the environmental damage. The technology and can be recommended for application.

Producing pigment fillers from dead chromium-aluminium catalysts

Chromium-aluminium catalysts are widely applied in organic synthesis, in particular in the processes of butane dehydration. Being poisoned with time, the catalysts become less active. Although chromium compounds in dead catalysts are highly hazardous for the environment, recovery has been uneconomical so far, for the known methods are ineffective and costly. Chromium in dead catalysts is a valuable, but toxic, component, especially Cr(VI). Besides chromium in terms of Cr_2O_3 (15.8 weight %), dead chromium catalysts contain, weight %: $\text{Al}_2\text{O}_3 - 75.0$; $\text{SiO}_2 - 7.1$; $\text{K}_2\text{O} - 3.5$; $\text{Fe}_2\text{O}_3 - 0.34$.

Chromium compounds are extensively used in anticorrosion pigments, for instance zinc chromate (Goldberg, 1976). We have substantiated the possibility of converting dead catalysts into anticorrosion pigment materials by employing either liquid or solid-phase methods. The presence of potassium in it indicates to the presence of chromium(VI). In the liquid-phase technology, we have studied the effect of acid/alkali concentration and temperature on chromium leaching to the liquid phase. Increasing sulphuric acid concentration was found to promote aluminium leaching. That the aluminium-containing core decomposes is confirmed by the fact that the rate of suspension filtration abruptly diminishes after leaching. Increasing the process temperature over 60°C initiates the chromium(III) leaching to solution, which decreases the chromium content in the final product deteriorating its pigment quality. When treating the catalyst waste with sodium hydroxide, we noticed that increasing NaOH concentrations and temperatures promoted chromium(III) liberation to solution. This, in turn, increased the content of water-soluble impurities, aluminates in particular. As the result of these studies, the following process parameters have been proposed:

- 1) sulphuric acid concentration – 50 g/l, process temperature 60°C , process time – 2 hours;
- 2) sodium hydroxide concentration - 5%, process temperature 60°C , process time – 2 hours (Fig. 2).

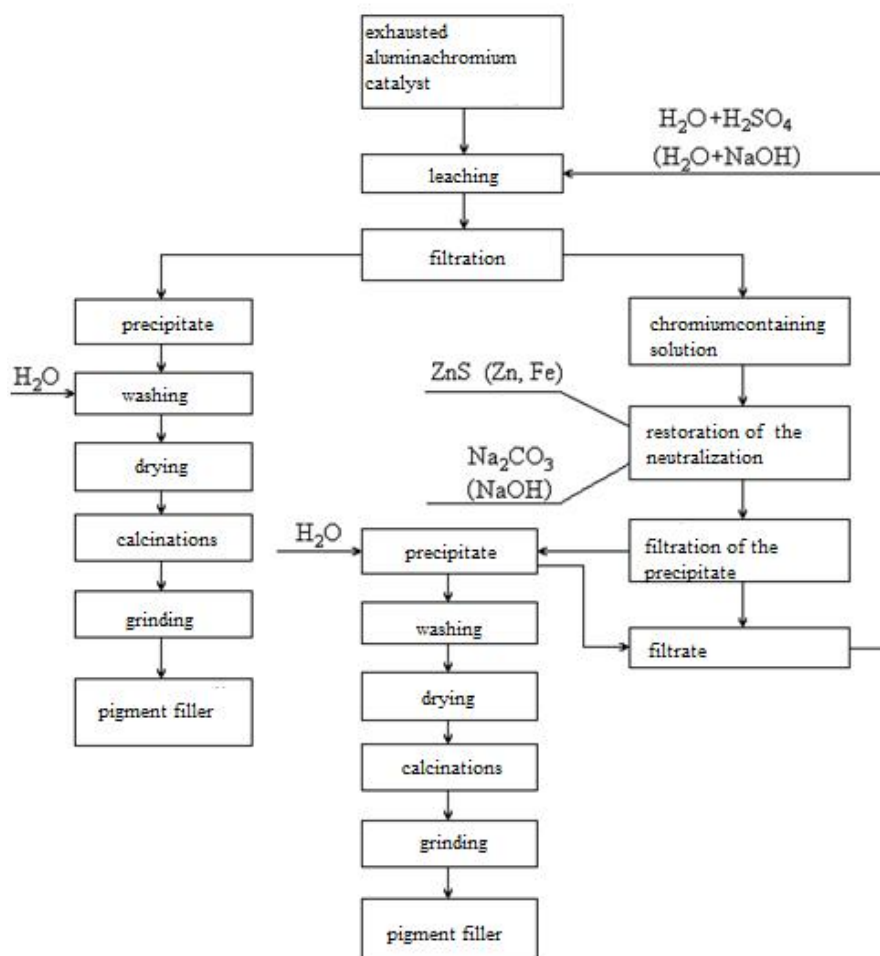


Fig. 2. Technological scheme for the processing of chromo-aluminium waste catalyst to produce coloured fillers for the liquid-phase method

The basis for the solid-phase method is heating of the mixture consisting of catalyst waste and calcium lime at 600-650°C, followed by grinding of the calcined product and surface modification. It has been demonstrated that desired quality can be achieved by adding 0.5-0.6% CaO to the waste bulk (Fig. 3).

The proposed methods for recovery of chromoaluminium catalysts are simple for technology and yield a high-quality, bright-green pigment filler having anticorrosion properties. At the same time, utilization of catalysts facilitates solving the problem of environment contamination with toxic chromium wastes. Colour intensity can be varied over a broad range by varying the charge composition. These products meet the requirements to pigments of both enamel and water-dispersed paints. The technology has been introduced at the Yarsintez SPA in Yaroslavl.

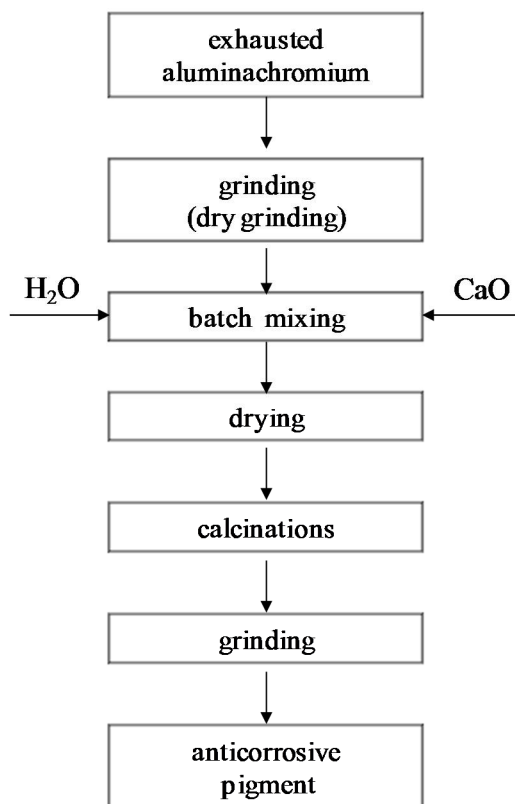


Fig.3 Technological scheme for the production of anticorrosive pigments by solid-phase method

Utilization of special magnet waste

Samarium-cobalt (SC) magnet rejects are highly interesting for recovery. We also have investigated several batches of neodymium-boron-iron (NBI) wastes (Kaluga) available as a dark-grey powder. The chemical composition of the wastes is presented in Table 4)

Table 4. Chemical composition of magnet production wastes

Waste	Component composition, weight %						
	Ln	Fe	Co	Al	Si	C	Moisture content, weight %
SC	35-45	0.1-0.3	50-60	-	-	1-4	3-6
NBI	23-30	36-52	3-13	0.4-0.6	0.1-0.3	5-6	4-12

Evidently, the method of processing had to be chemical due to different solubility of trivalent samarium (neodymium) sulphate and divalent cobalt (iron) sulphate in sulphuric acid media (Belenky and Riskin, 1974). This makes possible selective separation of rare earth elements (REE)

from other waste components. The parameters of technological operations yielding a REE concentrate are demonstrated in Fig. 4.

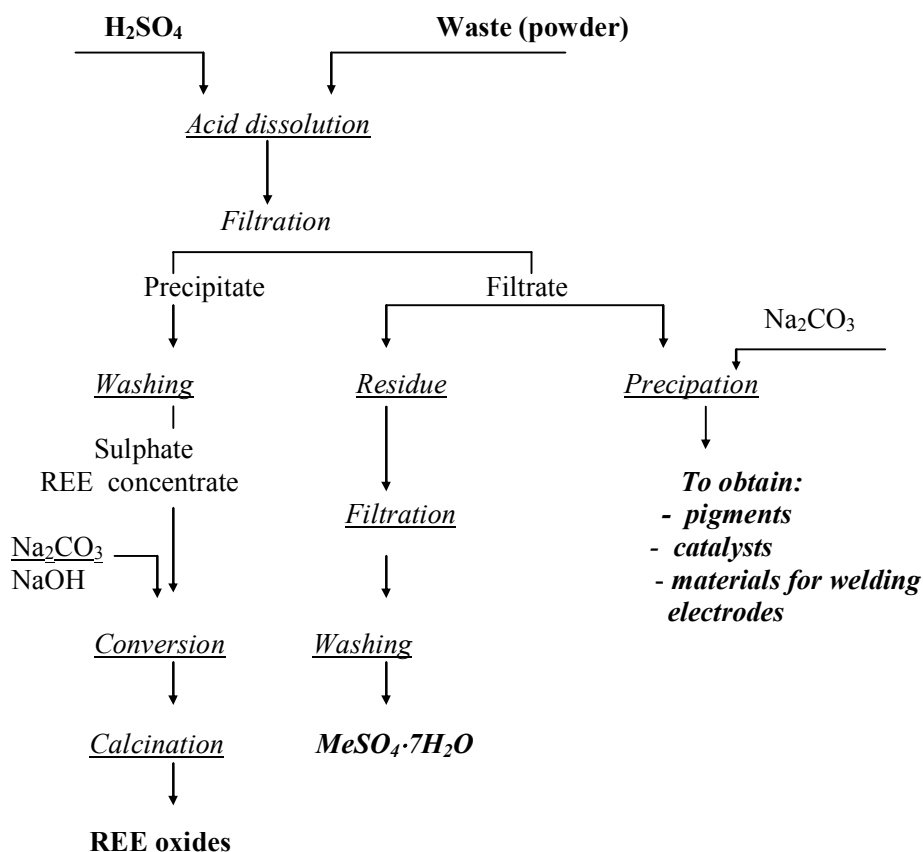
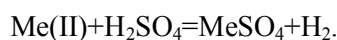
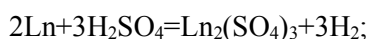


Fig.4 Basic technological scheme of special magnet wasters

In the flowsheet of waste utilization, the initial powders (unleached from the organic binder) interact with a sulphuric acid solution containing 350–370 g/l H_2SO_4 for SC and 450–470 g/l H_2SO_4 for NBI. The temperature of the reacting mass is 80–95°C. The powder is slowly added to a stirred sulphuric acid solution, which created conditions for removal of hydrogen-containing gas phase from the reaction zone. The component consumption corresponds to the mass ratio S:L=1:6–8. Principal chemical reactions involved in the method are follows:



Under these conditions, the samarium and neodymium sulphate compounds have low solubility, crystallizing in the form of hydrated sulphate salts: $\text{Sm}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ and $\text{Nd}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, where $n = 4-8$. Cobalt(II) and iron(II) remain in the sulphuric acid solution. The liquid phase is separated from crystalline precipitate by filtration; the latter is washed with hot water (70°C) on a filter at the ratio of S:L=1:0.25–0.5.

The sulphuric acid filtrates are evaporated under atmospheric conditions to separate cobalt(II) and iron(II) sulphate compounds. Excess sulphuric acid is removed by washing the precipitate with water. The composition of the resulting salts corresponded to the formula $\text{MeSO}_4 \cdot 7\text{H}_2\text{O}$. During pilot testing, 3 t of 'sulphate' REE concentrate were obtained.

It should be noted that, due to low-selective separation process, some of the REE in neodymium-boron-iron wastes were leached to the acid liquid phase together with iron(II). Conditions for utilizing such solutions to obtain coloured pigments, catalysts, and materials for welding electrode coatings have been investigated. These products were obtained from a hydrated precipitate (HP) extracted from sulphuric acid solutions by adding to it an alkali reagent (Na_2CO_3), up to pH 3-4.

The process occurs in an oxidative regime. The other parameters for HP precipitating are as follows: initial concentration iron in solution - 70-120 g/l Fe_2O_3 , temperature – 65-80°C, time – 12-18 hours. The extracted HP contains hydrated iron, neodymium and cobalt hydroxides with the element valence of 3. The pigment product is obtained by modifying the surface of HP particles with aluminium and silicium compounds (aluminium sulphate and sodium silicate). The modified precipitate is calcined at 750-800°C, with a resulting bright-brown, purplish product with fine hiding and thermal resistant properties. By varying the surface modification conditions and calcining temperature, it is possible to change both the colour and performance of the pigment, including its resistance to light, weather and heating, hiding property, etc. (Evdokimov, et al., 1994, Agafonov, et al., 2001).

The presence of rare earth element hydroxides in HP composition opens a possibility to apply it in the production of catalysts for hydrocarbon dehydration (Mukhlenov, 1979). In this case, HP is treated with a potash solution containing molybdenum; the treated precipitate is granulated and calcined at 600-650°C to fix the modifying agent on the HP surface. Pilot batches of the product have been tested for their structural-mechanical and catalytic properties. Dehydrated HP can also be used as a filler to the charge mix in welding electrode production. Adding small quantities of rare earth elements to the welding electrode coating composition improves the performance of welded connections. Heating and strain are known to hamper the grain growth in welded connections and alloys based on iron alloyed with rare-earth elements. Modification ensures a high level of plasticity, especially at negative temperatures. In work (Gerasimova, et al., 2006), a schematic diagram for the processing of special magnet wastes is presented.

Based on the example of a small group of objects of different composition and origin, the authors demonstrated the possibility and usefulness of the utilization of some wastes in the production of materials for building industries, beneficial from both economical and environmental considerations.

REFERENCES

1. Agafonov G.I., Kleshev D.G., Tolchev V.Yu., 2001. J. Paint-and-lacquer materials and their applications, 10, pp.41-43.
2. Belenky E.F., Riskin I.V. 1974. Chemistry and technology of pigments. M. Khimiya.
3. Bolshakov K.A. 1978. Chemistry and technology of rare and scattered elements. M: Vysshaya Shkola
4. Evdokimov A.V., Bykov E.A., Kleshev D.G. 1994. J. Paint-and-lacquer materials and their applications, 4, pp.31-32.
5. Fyodorov S.G., Nikolaev A.I., Brylyakov Yu.E., Gerasimova L.G., Vasilieva N.Ya. 2003. Chemical processing of mineral concentrates of the Kola Peninsula. Apatity KSC RAS.

6. Gerasimova L.G. 2001. Pigments and fillers from natural and technogenous titanium-containing resources. Apatity KSC RAS.
7. Gerasimova L.G., Nikolaev A.I. 1999. Composite and core pigments – new possibilities of synthesis and application. J. Paint-and-lacquer materials and applications, 4, pp.3-7
8. Gerasimova L.G., Nikolaev A.I., Safonova L.A. 1998. Pigments and fillers from thermal power plant ash. Rus. J. Applied Chemistry, 70, 5, pp.744-748.
9. Gerasimova L.G., Nikolaev A.I., Maslova M.V., Okhrimenko R.F. Utilization of magnet production waste containing rare-earth elements. 2006. J. Izvestiya Vuzov. Chernaya Metallurgiya, 5, pp. 37-39.
10. Goldberg L.V. 1976. Finished and semi-finished paint-and-lacquer materials. M. Khimiya
11. Kochergin A.V., Krasnobay N.G. 2003. Iron oxide pigments and pigmented fillers: market analysis and trends for natural resources utilization. J. Paint-and-lacquer materials and their applications, 1, pp.3-14.
12. Kuleshova I.D. 2002. ‘Talkon’ microtalc from Irkutsk – new fillers for paint-and-lacquer materials. J. Paint-and-lacquer materials and their applications, 12, pp.4-8.
13. Larionov V.P., Zorin E.E. 2003. Use of rare earth elements to produce cold-resistant construction materials. J. Welding production, 10, pp.42-44
14. Makarov V.N., Gerasimova L.G. et al. 2001. Utilization of copper-nickel ore dressing waste in pigment production In Building and technical materials from natural and technogenous sources of the Kola Peninsula. Apatity, KSC RAS.
15. Mukhlenov I.P. 1979. Catalyst technology. L. Khimiya.
16. Nikolaev A.I. 1991. Processing of unconventional titanium sources of the Kola Peninsula. Apatity: KSC RAS.