Available at www.scientevents.com/proscience/
ScientEvents
ProScience 2 (2015) 31-37
ProScience

Conference Proceedings
1st International Conference on Applied Mineralogy & Advanced Materials - AMAM2015

# Mineral waste recovered as pigments and fillers

Lidia Gerasimova, Marina Maslova*

*I.V.Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Kola Science Centre of the Russian Academy of Sciences, Apatity, Murmansk region, 184209, Russia*
**maslova@chemy.kolasc.net.ru*

## Abstract

Recovery of mining and dressing tailings has long been of global concern. The volume of mineral waste can be minimized by turning them into new materials, such as mineral composites used as components of building products. The paper discusses the feasibility of recycling apatite-nepheline ore, copper-nickel ore, and mica dressing wastes to produce white and color pigments, weather-resistant paints and paint primers, fillers for rubber and plastic compounds, and anticorrosion paint primers. The work involved researching of the waste initial compositions, chemical process parameters and optimal conditions for synthesis of products with tailored properties, and outlining of the application areas.

*Keywords: Mineral waste, Utilization, Apatite, Nepheline, Phlogopite, Pigment, Filler.*

Nowadays, with natural resources for manufacture of pigments and filler compounds either running out or inaccessible without much capital investment, it is worthwhile considering such sources as dressing tailings of current production.
Appreciable diminishing of the amount of current waste can be achieved by a large scale processing. The potential consumers are the industries operating with substantial material flows, including civil and defense engineering or manufacture 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.

Research is also aimed at developing composite pigments containing titanium, iron, aluminum, silicon, and calcium compounds in different combinations (Gerasimova, 2001;

ISSN: 2283-5954
Selection and peer-review under responsibility of AMAM2015 Scientific Committee
DOI:10.14644/amam.2015.006

Gerasimova & Nikolaev, 1999; Golberg, 1976; Larionov, 2003). As a rule, the properties of an entire composite are determined by those of the coating pigment component represented by known synthetic or natural fillers such as calcite, alumina, silica, and talc. Thus coated materials acquire both pigmenting and filling properties. The former tincture the products, imparting them with a more attractive appearance, the latter - improve their technical characteristics including the resistance to heat, light and aggressive media, high loads and bending strengths, etc. Mineral composites can be produced from multicomponent mineral wastes of mining and dressing enterprises (Kuleshova, 2002).

## 1. Recovery of apatite-nepheline ore dressing wastes

The object of research was the foam product of nepheline flotation from the ore dressing process, yielding apatite and nepheline concentrates at Apatit JSC, Murmansk region, Russia. The foam is mostly unprocessed and dumped as a water suspension. The nepheline tailings (NT) contain 25% nepheline, 4% apatite, and also titanite, egirine and feldspar minerals.

We propose recycling the nepheline using a method combining the chemical and dressing operations, yielding both enriched mineral concentrates and various low-cost and scarce synthetic products convertible to plastic, paintwork and building materials, and also agents for drinking and sewage water treatment from suspensions and deleterious impurities, including radionuclides.

The new technology is based on the method of cascade reactions (Gerasimova & Maslova, 2012). Each of the stages occurs under strictly controlled conditions, so that the reaction products are either wholly isolated as target products or sent to further processing. The main chemical reactions occurring in this process are:

$$(NaK)_2Al_2O_32SiO_2 + 4H_2SO_4 = (NaK)_2SO_4 + AI_2(SO_4)_3 + H_2SiO_3 + 3H_2O \quad (1)$$

nepheline

$$Ca_5(PO_4)_3F + 5H_2SO_4 = 3H_3PO_4 + HF + 5CaSO_4 \quad (2)$$

apatite

$$CaSiTiO_5 + 2H_2SO_4 = TiOSO_4 + CaSO_4 + SiO_2 + 2H_2O \quad (3)$$

titanite

$$AI_2(SO_4)_3 + 2H_3PO_4 = 2AIPO_4 + 3H_2SO_4 \quad (4)$$

$$TiOSO_4 + H_3PO_4 = TiOHPO_4 + H_2SO_4 \quad (5)$$

When treated with sulphuric acid, the components are gradually leached out to the liquid phase to be finally converted to new compounds forming target products  either individually or in combination with other compounds. The products obtainable with the new method are listed in Table 1.

Table 1. Characteristics of the products obtained from NT.

| Product | Components | Field of use |
|---|---|---|
| Product I | Colloid solution of aluminum and silicon  a coagulating-flocculating agent | Thickening of suspensions with a finely divided solid phase. Water purification from oil, suspensions, iron, etc. |
| Product II | Acid aluminium phosphate, silica gel | Anticorrosion compounds on the organic and water bases |
| Product III | Titanium hydrophosphate or its composite with silica gel | Sorption purification of toxic liquid effluents |
| Product IV | Calcium sulphate, amorphous silica, titanium dioxide | Dry building composites for whitewashing |
| Product V | Sphene and egirine concentrates | In the production of pigments, weather-resistant paints and paint primers |

The minerals, unaffected by sulfuric acid under these conditions, are subjected to magnetic separation. The resulting products are titanite and egirine concentrates with mineral contents over 90%. Fig. 1 demonstrates a multivariant schematic diagram for the production of these concentrates.

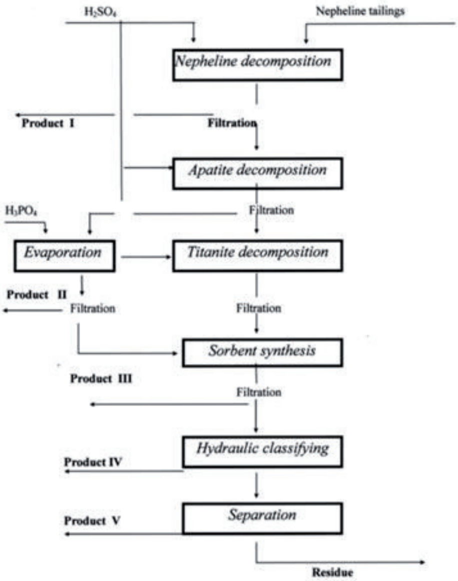


Fig. 1. Schematic flowsheet of nepheline tailings recovery.

Sphene concentrate contains titanium, but in lower contents compared to the industrially processed ilmenite concentrate. Therefore there is no economic benefit in processing of sphene for pigment titanium dioxide. However, by employing simple methods such as fine grinding, it is possible to obtain titanium dioxide-based pigment fillers with attractive properties (Fig. 2, Table 2).

The pigment filler is a fine light-beige powder, non-toxic and fire- and explosion-proof. It is made from sphene containing 35-38% $TiO_2$ and can be used in manufacture of paint-and-lacquer and building materials, rubber, plastic and ceramic. We propose using it as a substitute for pigment titanium dioxide in paintwork materials of a wide colour range, building materials, including laminated flooring boards, linoleum and dry building compounds, dielectric rubber items, heat-resistant ceramic tiles, etc.

## 2. Pigment fillers from olivine ore dressing waste

Olivine concentrate, extractable via strong and weak magnetic separation from ores of the Khabozero deposit (Murmansk region, Russia), is used in manufacture of refractory materials. The marketable olivine concentrate is represented by the heavy fraction. As for the light fraction (yield ~25%), it is magnetically separated into two fractions of which one is magnetic (reddish black), containing 18.70% $Fe_2O_3$, and the other is non-magnetic (white), with a mere 0.42% $Fe_2O_3$. As revealed by XRD analyses, the bulk of the white concentrate is represented by lizardite (LC), ($Mg_3Si_2O_5(OH)_4$) - a mineral variety of serpentine. Using calcination, LC is converted to forsterite ($Mg_2SiO_4$) and enstatite ($Mg_2[Si_2O_6]$). The reddish-black fraction mostly consists of antigorite ($(Fe, Mg)_3Si_2O_5(OH)_4$.-(AC). Calcined antigorite contains forsterite, magnesioferrite ($MgFe_2O_4$, a mineral of the ferrispinel group), magnetite, and $MgSiO_3$.

Table 2. Physical-technical properties of a filler obtained from sphene.

Fig. 2. SEM-image of filler particles sized 8 $\mu$m.

| | |
|---|---|
| Appearance | Light-beige powder |
| Density, kg/m$^3$ | 2900 |
| Bulk weight kg/m$^3$ | 800-1150 |
| Moisture content, % | Not more than 1 |
| Oil absorption , g/100g | 15-20 |
| Hiding property g/m$^2$ | 55-65 |
| Content of water-soluble salts , % | Not more than 0.5 |
| Oversize product ( sieve 0045), % | Not more than 0.1 |
| Refraction coefficient | 2.0 - 2.1 |
| Content of elements, oxides, $TiO_2$,% | 36 - 38.5 |
| $SiO_2$ | 29 - 3 |
| CaO | 29 - 30 |

We examined the following properties of LC and AC essential for pigment fillers: whiteness, hiding property, oil absorption, content of water-soluble salts (WSS), and pH of the aqueous extract. For example, the finely ground LC appears whiter with diminishing of the grain size owing to increasing reflection power of expanding surface area. The response of the above-listed properties to heating was studied by calcining LC and AC at 200, 500, and 800°C and recording the weight losses (Table 3). After calcination, the LC colour becomes less intense (yellow) than that of AC, which turns reddish-brown at 800$^0$C. In both cases, the colour changes due to Fe(II) oxidation to Fe(III).

Neither LC nor AC dispersions in paint oil are acceptable as pigments, the former having poor coating features, the latter producing a too thick coating. However, due to their low oil absorption and WSS values both LC and AC powders can be used as primers and putties in the construction industry or as inert cores for pigment fillers of a shell-type structure.

Table 3. Main characteristics of pigments from LC and AC.

| Property | Lizardite concentrate | | | | Antigorite concentrate | | | |
|---|---|---|---|---|---|---|---|---|
| | Without calcination | Calcined at °C | | | Without calcination | Calcined at °C | | |
| | | 200 | 500 | 800 | | 200 | 500 | 800 |
| LOI,% | - | 2.94 | 6.19 | 19.2 | - | 3.59 | 7.33 | 1 |
| Color | Yellowing-whitish | | | | Light-brown | | Tawny | |
| WSS, % | 0.82 | 0.53 | 0.64 | 2.44 | 0.55 | 0.77 | 0.59 | 1.01 |
| pH of aqueous extract | 7.34 | 7.72 | 7.70 | 11.6 | 7.62 | 7.74 | 7.96 | 8.18 |
| Oil absorption, g/100g | 32.2 | 32.2 | 32.2 | 41.4 | 32.2 | 41.4 | 36.8 | 41.4 |
| Hiding property, $g/m^2$ | - | - | - | - | 233.4 | 187.9 | 136,1 | 136 |

## 3. Recovery of copper-nickel ore dressing wastes

Owing to fairly high contents of layered silicates, the copper-nickel dressing tailings of the Kola Mining and Metallurgical Company (Murmansk region, Russia) can be converted to quality fillers (Makarov et al., 2001). In this work, we studied the waste of magnetic separation with the following mineral composition, wt. % (Table 4):

Table 4. Mineral composition of the waste.

| | | | |
|---|---|---|---|
| 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 naturally light-grey or light-brown after calcination at 850 °C, with a whiteness index of not higher than 64%. However, admixing with an organic binder improves the product s coating properties relating it to the pigment filler class (Fedorov et al., 2003). By using the fine fraction (<28 μm) of the light-grey product as a colouring pigment shell, we obtained coloured pigment fillers in both liquid and solid-phase regimes. The resulting colour shades were intense and uniform due to lamination of the core structure and to the high surface area (Kochergin & Krasnobay, 2003).

The quality of the filler is unaffected by sulphides present in copper-nickel dressing wastes. Moreover, the sulphides make the product brighter and more resistant to atmospheric action (such as light, water, etc.). Table 5 presents the synthesis parameters and main properties of the pigment fillers which can be satisfactorily applied in coloring compositions (Gerasimova & Maslova, 2012). The product range can be extended via pre-treatment (mechanical activation) and coating with flatting agents (Fe, Ni, Co, etc.).

Table 5. Manufacturing conditions and properties of pigment fillers.

| **Manufacturing conditions** | | **pH** | **WSS,** | **HP** | **Color** |
|---|---|---|---|---|---|
| Addition to initial sample, % | Heat treatment, °C | **of aqueous extract** | **%** | **g/cm$^2$** | |
| - | - | 7.32 | 2.56 | 295.3 | Light-grey |
| - | 150 | 6.60 | 0.56 | 250 | Light-brown |
| - | 850 | 7.25 | 0.28 | 113 | Light-brown |
| $CoCl_2$ - 2.5% | 900 | 7.37 | 0.3 | 84.5 | Dark-grey |
| $FeSO_4 \cdot 7H_2O$-- 10% | 500 | 7.34 | 2.1 | 12.5 | Brown (bright) |
| -«- | 850 | 7.46 | 1.4 | 17.5 | Reddish-brown |
| $Fe_2NiO_4$- 2.5% | - | 7.20 | 0.5 | 20.2 | Light-brown |
| $Fe_2NiO_4$-5% | - | 7.31 | 0.35 | 27.7 | Brown |

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

## 4. Recovery of mica process waste

Mica is mined as large phlogopite and muscovite sheets used in radio electronics and radio engineering. Smaller mica flakes are not utilized nowadays, awaiting the development of new technologies. However, it has long been known (Trotignon et al., 1992) that, actually, the size of mica flakes is uncritical when producing pigments lacquer-and-varnish, rubber and plastic extenders. Moreover, smaller mica flakes are preferable in this case due to lower power consumption at splitting and grinding operations.

In our experiments we examined the mica dressing tailings of the Kovdor deposit for the possibility of turning them into pearl pigments. The starting material (phlogopite $KMg_3[Si_3AlO_{10}](OH)_2$) with particle sizes of 0.2-2mm was subjected to electrochemical splitting (Gershenkop et al., 2001). It is known that an important stage in pearl pigment technology is depositing of a titanium or iron hydrated shell on the surface of fine mica particles. Deposition is usually effected via thermal hydrolysis of suspensions consisting of sulphate or chloride solutions of titanium and mica. Instead, the authors have proposed an electrochemical process conducted in an electrodialysis cell with a MA-40 anion-exchanging membrane. Mica particles act in the catolyte as crystallization centers for the solid phase of titanium(IV) hydroxide emerging during the electrohydrolysis of titanium(IV). The hydrated shell either creates a uniform coating or forms swellings at the most active places, such as edges. Besides, the titanium phase can precipitate individually, which also improves the pearl pigment quality. Electrohydrolysis terminates when the pH of the catolyte achieves 6-6.5. Compared to thermal hydrolysis, this process consumes much less water and, consequently, releases much less acidic waste. After drying, the precipitate is calcined at 600-800 °C. The resulting product is a fine-grain silky powder with a peculiar pearly shine. We have determined the optimal conditions for depositing of uniform coatings over the entire flake surface.

The results obtained indicate that mineral wastes can be recovered as materials for the building and lacquer-and-paint industries, the product range depending in each case on the feed composition.

## References

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, 196 pp.

Gerasimova L.G (2001). Pigments and fillers from natural and technogenous titanium-containing resources. Apatity: KSC RAS, 96 pp.

Gerasimova L.G., Nikolaev A.I. (1999). Composite and core pigments – new possibilities of synthesis and application. PLM and their applications 4, 3-7.

Gerasimova L.G., Maslova M.V. (2012). Recovery of mineral waste in the production of pigments and fillers for the building industry. Alitinform, 4-5, 102-104.

Gershenkop A.Sh., Gerasimova L.G., Khokhulya M.S., Zhdanova N.M., Okhrimenko R.F. (2001). Preparation of flaky pearly pigments. Inorganic Materials 37, 531-534.

Goldberg L.V. (1976). *Finished and semi-finished paint-and-lacquer materials*. M. Khimiya, 630 pp.

Kochergin A.V., Krasnobay N.G. (2003). Iron oxide pigments and pigmented fillers: market analysis and trends for natural resources utilization. PLM and their Applications 1, 3-14.

Kuleshova I.D.(2002). Talkon–microtalc from Irkutsk –new fillers for paint-and-lacquer materials. PLM and their Applications 12, 4-8.

Larionov V.P., Zorin E.E. (2003). Apply of rare and rare earth metals for cold-resistant construction materials. Welding production 10, 42-44.

Makarov V.N., Gerasimova L.G, Bastrikina S.A. (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, 29-36.

Trotignon J.P., Demdoum L., Verdu J. (1992). Effect of mineral fillers in low concentration on the mechanical properties of polymeric materials. Part 1: Static and fatigue fracture of polypropylene, qualitative aspects. Composites 23, 313-318.