Mining Waste Complex Research and Development of Technologies for their Use in Georgia

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Abstract. In 1996, Georgian mining and extractive industry moved to a new stage as a result of the adoption of a new law on subsoil, which prepared grounds for the development of a legislative framework regarding the use of country's subsoil and created new economic settings for the industry. Mining and extractive industry play a significant role in Georgia's sustainable economic development. From 1999 through 2020, the output value of the industry (excluding non-renewable energy resources: coal, natural gas and oil products) is estimated at of 5,6 billion Lari (GEL). The majority of deposits of mineral resources in Georgia are mainly small and medium in size. Considering the current rate of their exploitation, within 15-20 years their majority will be exhausted. Over time, the country's economy will face a serious problem as it will need to import raw materials. It is therefore important to look for feasible technologies for the application of unconventional raw materials, namely secondary raw materials that come with essential mineral resources. This will allow to maintain the potential of mineral resources of the country. The work presents the outcomes of the Mining Institute's current studies on qualitative, quantitative and assimilative technologies and possibilities of the application of mining waste as secondary natural resources. Research methodology is based on the principles of Green Economy that implies linking mining and extractive industry to circular economy, aiming at rational assimilation of natural resources by applying the 3R (reduce, reuse and recycle) approach. Within the frames of the study, technologies were developed for obtaining construction, glass and porcelain raw materials (from spoiled rock layers stored and extracted from operating open pit mines of the Chiatura manganese and Bolnisi ore deposits/queries), along with those for manufacturing products with such materials.

1. Introduction

Georgia's mining and the extractive industry's development history covers a number of centuries. Georgian Tribes, like Chalybes, Mossynoeci and Tabals are recognized by many scientists as those living in the motherland of mining, extracting works and metallurgy [1].

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The development of mining and the extractive industry of Georgia in the modern age started in XIX century that is related to Tkibuli hard coal (1846) and Chiatura manganese ores assimilation (started in 1879). 1974 is also considered as the significant date, as since then gold and silver production took place in Bolnisi ore region. In 80s of previous century, mining and the extractive industry's share amounted in 10-12% of country's production, that in average was equal to 400 million dollars and about 16-17 thousand man was employed in it [1,2]. The development of mining and extractive industry was encouraged by the fact that Georgia is rich in natural resources despite a small territory it occupies (69 700 km²). The country has 960 deposits of solid mineral resources, such as gold, silver, lead and zinc, barite, manganese, hard coal, diatomite, marble, tuff, construction and other mineral raw materials [3]. Mining and the extractive industry was especially influenced by complexities regarding of Georgia's transformation into independent country and transition on the market economy. During of 90s of the previous century the field's condition was critical, which was caused by loss of production market and investments' attraction issues. Nearly all the enterprises were suspended or were working at 3-10% of their project capacity during that period [2].

In 1996, Georgian mining and extractive industry moved to a new stage as a result of the adoption of a new law on subsoil, which prepared grounds for the development of a legislative framework regarding the use of country's subsoil and created new economic settings for the industry [2]. During the process of complex and delayed privatization of state mining enterprises, investors' interest in developing and merging mining enterprises increased. The value of the production output of the mining and extractive industry in 2020 amounted to 1,098.0 billion GEL, compared to 13.5 million GEL in 1999 [4]

Deposits of natural resource in Georgia are small and medium size. Judging by the speed of extraction and mining, most of them will expire within the next 15-20 years, which will create a serious problem for the country's economy, resulting in a need to import raw materials from other countries. It is therefore important to find rational technologies for the use of non-traditional raw materials materials that come with essential mineral resources. This will allow to maintain, yet partially, the potential of mineral resources of the country.

2. Analysis of existing condition

Currently, when evaluating mineral resources, so-called "waste rocks" - accessory and nonconventional resource, that underlie, cover and embed essential minerals are usually neglected. The results of the studies show, that more than 85% of industrial wastes in Georgia comes on mining waste . Mining wastes cause direct and indirect negative impacts on the environment. Direct impacts result in deterioration of soils, changes in landscapes, decreased availability of agricultural lands and forests, destruction of the vegetation, etc. Indirect impacts cause reduction of soil fertility, deterioration of conditions for plants growth, emissions of dust and harmful chemicals, infiltration of polluted waters and deterioration of the quality of surface and underground waters, changes in hydrological regime.

One of the problems obstructing the development of mining sector in Georgia is the lack of observance by mining companies of best practices related to the rational use of mineral resources and protection of the environment. Waste rock dumps and tailings of existing mining companies (Chiatura manganese deposit and Bolnisi deposit: Madneuli, Sakdrisi, Kvemo Bolnisi, Bektakari) occupy tens of thousands of hectares of agricultural and forest land, Figure 1. They contain quartz sandstones, Maikopian clays, quartzous tuffs, pelitic tuffs, albitophires, tuffalevrolites, igneous quartzites and porcelain, which can be used as secondary raw materials as evidenced by different studies. These materials, the potential of which remains



underestimated, can be used for manufacturing silicate bricks, glass, sorbents, cement-concrete aggregates, and porcelain items. Their application in industry will contribute to the treatment of mining waste, improvement of local ecosystems and sustainable development.

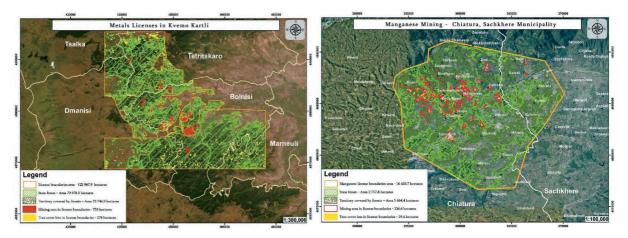


Figure 1. Territorial maps of mining appurtenance of goldpolymetals from Bolnisi ore region and Chiatura manganese ore

3. Macroscopic and microscopic study of mining waste

For the purposes of the present research, we adjusted an open pit mine in Bolnisi, where gold and copper ores have been extracted since the 1980s. 4 dump and 2 tailing disposal sites are located at the open pit mine production site Figure. 2.

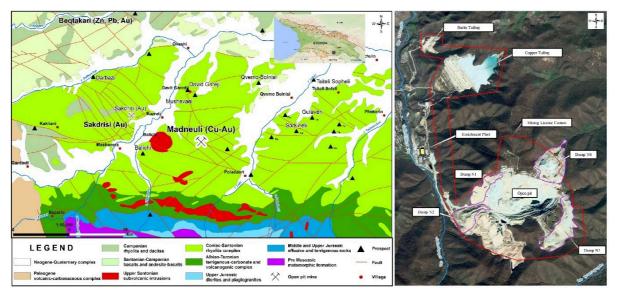


Figure 2. Geological map of Bolnisi Deposite [5] and Madneuli open pit mine (Bolnisi, Georgia)



3.1. Results of macroscopic and microscopic research

Samples of tuff turned into quartz, rhyolites, albitophyres, tuffaceous siltstones and oreless quartzites were collected from dump sites. The thin sections were made of rock layer samples, which were then observed through macroscopic and microscopic methods according to lithologic research. RADICAL RPL-3B; SP 4/0.10. microscope was applied during research

Sample 1. Tuffs turned into quarz have whitsh to grey color; they are solid, have pinkish to rusty coatings and is not reactive to hydrochloric acid. The rock layer in microscope is homogenous, it is fully presented by small grains of quartz and feldspar, comparatively big crystals and smallest scales of mica are rarely observed, excess amount of clay mass and iron hydroxide are met by sections; rock layer is porous, pores are free, Figure 3.

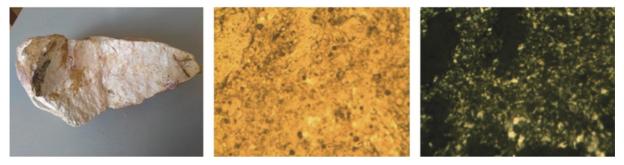


Figure 3. Sample of tuffs turned into quartz

Sample 2. Oreless quartzites are reddish to grey in color. They do not react to hydrochloric acid. In microscope, the rock layer is fine-grained, on tenth muddy, almost isotropic background there are lots of different sized quartz and feldspar grains and of scales mica; the rock layer mostly consists of sections replaced by secondary material (seriate, iron dioxide), often whole fragments are replaced by material, Figure 4.

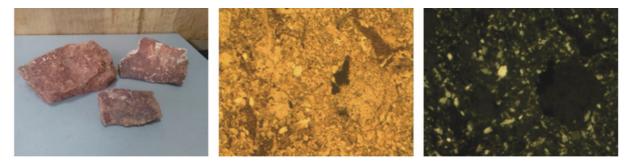


Figure 4. Sample of oreless quartzites

Sample 3. Albitophyres are brownish to flesh colored, solid, are not reactive to hydrochloric acid. The rock layer in microscope is fully presented with small grained quartz and feldspar mass, which rarely consists of comparatively big grains of quartz, Figure 5.



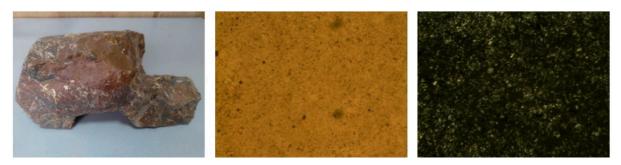


Figure 5. Sample of albitophyres

Sample 4. Tuffaceous siltstones are light grayish, solid and they do not react to hydrochloric acid. The rock layer in microscope is homogenous, fine-grained, muddy and in the almost isotropic background are seen the smallest grains of quartz and feldspar, increased capacity of clay mass are met as sections, the rock layer is porous and the pores are free, Figure 6.

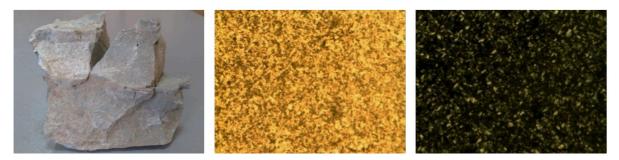


Figure 6. Sample of tuffaceous siltstones

Sample 5. Rhyolite is grey, different-sized enclaves of segments can be clearly seen; they do not react to hydrochloric acid. The rock layer in microscope is altered, muddy, with porphyric structure, in the background of fine-grained basic mass, there are lots of different sized porphyric separations, which are mainly represented by quartz and feldspar, small crystals of mica are rarely observed, Figure 7.

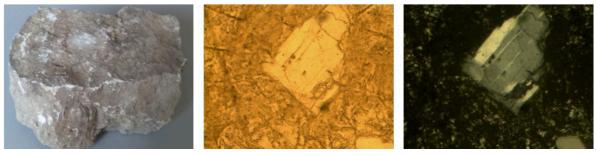


Figure 7. Sample of rhyolite



For the current stage of research, our target was to work out the technologies to receive the glass raw materials and glass products from the mentioned spoiled rock layers. the studies for obtaining of construction, ceramic and porcelain raw materials will be performed on the next stage.

4. Technology of making a glass and glass products from rock layers

4.1. Granulomatous and silicate analysis of the samples

With existing experience and on the basis of lithologic analysis, we adjusted oreless quartzites to receive the glass raw materials and glass products. Representative sample of 80kg mass oreless quartzite monoliths taken from the dump place were broken into small particles with sizes lesser than 2.5mm, which was crushed by jaw crusher. After of their drying on the air, the sub-patterns were separated for technological, granulometric and chemical analysis.

The study of granulometric composition was performed by sieve analysis method, the results of which are given in Table 1.

Nº	Sieve fraction, mm	Mass content of fraction, %	Mass content of SiO ₂ , %	Picking up of SiO ₂ , %		
1	+2.5	-	-	-		
2	-2.5+1.25	33.419	76.07	32.94		
3	-1.25+0.63	5.427	84.02	5.91		
4	-0.63+0.315	17.25	83	18.55		
5	-0.315+0.16	8.859	78	8.95		
6	-0.16+0.08	8.847	80	9.17		
7	-0.08+0.04	-	-	-		
8	-0.04+0	26.198	72.13	24.48		
9	-2.5+0	100	77.18	100		
10	With balance		77.18			
11	By chemical analysis		79.11			

Table 1. Granulometric composition of technological sample.

Based on granulometric composition, the following fractions were adjusted for silicate analysis: 1) - 1.25+0.63mm; 2) -0.63+0.315mm. The complete silicate analysis were performed the outcomes of which is given in Table 2.

Table ? Desults of silicate analysis

	Table 2. Results of sincate analysis.													
№	Sample title	Mass content of the components, %%												
		Moisture %	SiO ₂	Fe_2O_3	Al_2O_3	TiO ₂	Mn0	Ca0	MgO	Na ₂ O	K ₂ 0	<i>SO</i> ₃	$P_{2}O_{5}$	Hardening loss
1	-1.25+0.63 mm	0.46	84.02	6.02	4.01	0.2	0.02	3.8	0.4	0.12	0.52	0.04	0.07	1.3
2	-0.63+0.315 mm	0.46	83	6.08	4.13	0.3	0.02	4	0	0.16	0.62	0.05	0.06	1.5



4.2. Technology of making a glass and glass products

As a result of the analysis conducted for technological examinations with a view to determining the possibilities of the use of main glass components - 1,25+0,63mm sample was chosen. As it is obvious from the data given in Table 2, the raw materials (with SiO_2 composition) to be studied are acceptable in glass manufacturing as substitute of quartz sand; as of aluminum and iron oxides - the significant parts of glass composition, their amounts (especially Fe_2O_3) makes it difficult to fully replacem quartz sand in glass charge by calcite to be studied. Iron oxides (in an amount of 1-1,5 mass.%), due to iron valency, grant dark greenish to yellowish or dark greenish to sky-blue color to glass, but in case of 2 mass.% and more - glass becomes blackish and dark black. Besides, glasses with high concentration of iron are very sensitive to the crystallization ability, which makes their processing by glass moulding automatized machines difficult. We have chosen standard bottle glass composition $(SiO_2 - R_2O_3 - RO - R_2O$ system) for experiment purposes. It is possible to have a high iron oxide composition in the bottle glass compared to all other glasses, because it is used as active coloring component in these glasses. In case of higher (> 3 mass. %) composition of iron oxides, it is possible to obtain a black, sparkling, mirror-like surfaced, non-transparent marblite glass, which is used in construction, in particular - in production of decorative plates. We have conducted an experiment on glasses of two basic composition by applying different coloring agents. In one case, we have taken 100% quartzite to be studied instead of SiO₂ in marblite glass charge, and in the second case - we have tried to reach 1 mass. % in experimental colored glass to near up composition used in bottle manufacturing. The composition of experimental charge and glasses is given in Table 3.

N⁰	raw material, gr.	Oxides, mass.%									
JN⊻		SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K_2O	SO_3		
	Planned										
	composition of the	70	2,0	0,2	10	2	15	1	-		
	glass										
<u>6</u> 1	quartzite, 83,3	70	3,34	5	3,16	0,33	0,1	0,43	-		
	<i>CaCO</i> ₃ , 12,3	-	-	-	6,84	-	-	-	-		
ssJ	Na ₂ CO ₃ , 28,8	-	-	-	-	-	16	-	-		
Glass №1	Σ (100,2)	70	3,34	5	10	0,33	16,1	0,43	-		
•	100%-ზე (100,0)	69,86	3,33	4,99	9,98	0,33	16,06	0,43	-		
	quartzite, 16,7	14	0,7	1,0	0,64	-	-	0,09	-		
	quartz sand, 56	56	-	-	-	-	-	-	-		
ğ	$Al_2O_3, 1,3$	-	1,3	-	-	-	-	-	-		
Ž	<i>CaCO</i> ₃ , 16,85	-	-	-	9,36	-	-	-	-		
Glass Nº2	<i>Na</i> ₂ <i>CO</i> ₃ , 28,48	-	-	-	-	16,0	-	-	-		
5	$K_2CO_3, 1,57$	-	-	-	-	-	1,0	-	-		
	Σ (100,1)	70	2,0	1,0	10	-	16,0	1,1	-		
	On 100% (100,0)	69,93	2,0	1,0	9,99	-	15,98	1,1	-		
Glass No3 - 100 mass.% of Glass No2 was added with 0,8g. $K_2Cr_2O_7$											
Glass	5 №4 - 100 mass.% of	Glass №2	was added	l with 1,5g.	MnO_2						
Glass	5 №5 - 100 mass.% of	Glass №2	was added	l with 2g. su	ılphate						

Table 3. Calculated chemic	al composition	of glasses
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Small (up to 0,1 mass. %) amount of oxides in quartzite composition is not calculated. As indicated in the table, in the case of application of 100% calcite as raw material of SiO_2 , it brings into glass 3,33 mass.% amount of Al_2O_3 , which will not have a negative impact on glass-making manufacturing mode. 5 mass. % of Fe_2O_3 brought into to make a marblite glass does not need an additional coloring agent.

To obtain colorful but darker glasses, it is necessary to reduce the amount of iron oxide to 1 mass.%. In such case, the amount of quartzite - the raw materials to be studied is being decreased to 17 mass. %, the rest amount of SiO_2 is being filled up with double enriched quartz feldspar sand of Bajiti ore deposit (Georgia). Decrease of iron oxide up to 1 mass. % in the glass allowed us to try to paint the main mass of the glass by $K_2Cr_2O_7$, MnO_2 , additive of Na_2SO_4 .

 Cr_2O_3 is coloring agent in $K_2Cr_2O_7$ glass and together with iron oxide it gives green colour to the glass, and MnO2 - Mn2O3 together with iron oxide gives us greenish to yellowish color. It is known to paint the glass with iron and sulphur at a time giving us a yellowish-orangish color, but in our case, because of a large amount of iron, it is possible that the desired effect will not be achieved. We started the lab experiment by calculating glass charges and glass compositions on the basis of which the dosage of charges (given in the Table 3) was established, then mixed with charges acquired until they become fully homogenous. The obtained homogenous charges were placed in 100g capacity corundum glass pots. The charges were boiled in the neutral area with a sylitol heating electric furnace. Temperature in the furnace rose from the room temperature to 1520-1530°C, delay - 30-35 minutes. Boiled homogenous glasses were casted under free fall method, at maximum temperature. In order to prevent cracking of glasses in heated iron forms, the samples of glasses obtained were burned in the muffle furnace at 560-570°C and cooled naturally in the disconnected furnace. All the glasses were boiled and cast with good flow, freely, with normal viscosity, were spread until the fill of forms, are cleaned and homogenous. We obtained homogenous melts, equally painted in different colors.

4.3. Description of received samples of glass

The figure 8 below shows the samples of glasses made by using an oreless quartzites and the quartz sands.



Figure 8. Samples of received glasses

Glass N = 1 - non-transparent in volume, with black, sparkling, mirror-like surface, homogenous without gaseous enclaves.

Glass №2 - transparent, pure, sparkling surface without enclaves, yellowish to green color. Decrease of iron oxide composition up to 1 mass.% made glass transparent and painted it in bottle glass color.



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Glass №3 - transparent, effective green, pure, sparkling surface. Combination of chromium and iron oxides has painted it more intensively comparing to №2 glass.

Glass №4 - with pure, homogenous, sparkling surface, light honey-colored that is resulted by combination of manganese and iron oxides.

Glass №5 - with homogenous sparkling surface, less intensively painted, with light green to yellowish color that is the result of unity of iron and sulphur.

5. Conclusions

- Qualitative, quantitative and assimilation technologies and possibilities of using mining and extractive industry wastes as secondary natural resources in manufacturing is important for the sustainable economic development and rational assimilation of environmental resources;
- It is important to develop mining and extractive industry by taking into account best practices, minimizing long-term application and environmental impact of mining resources;
- glass raw materials and glass acquisition technologies from the spoiled rock layers (stored at the dump places of ore`s open pit mine) were processed;
- The study results can contribute to the transition of Georgia's mining and extracting industry into an an industry modelled on circular economy, thus promoting the development of green economy in the country.

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