GOSPODARKA SUROWCAMI MINERALNYMI

Tom 23 2007 Zeszyt 4

VLADIMIR CABLIK*

Characterization and applications of red mud from bauxite processing

Key words

Red mud, pigment, bauxite

Abstract

This work describes the characterization of red mud – a waste generated by the Bayer process in the aluminium industry – which causes environmental problems. Residue of the alumina leaching from bauxite was analyzed for mineral compositions of the mineral ore and its residue for chemical composition, density, and grain-size composition. The residue was calcinated and finally tested as a pigment for use in the building material industry. The test blocks were tested on the compressive strength.

Introduction

The Birac Alumina Industry is located in eastern Bosnia, 25 km west of Tuzla and 85 km SW of Sabac, Serbia. Bauxite is transported to the Industry by road and railway mainly from local sources (Vlasenica, Krunici, Mrkonjic) and from Niksic, Montenegro, or from India.

The Birac Industry extracts alumina mainly from monohydrate bauxites by the Bayer process. A large amount of the red mud waste that pollutes streams is an environmental problem for the industry and the local community.

Bauxite residue (also known as red mud) is a by-product of the Bayer process. The amount of the residue generated, per ton of the alumina processed, varies greatly with the type of the bauxite ore used from 0.3 ton to 2.5 tons for high and very low-grade bauxites, respectively.

* Ph.D. Eng., VSB-Technical University of Ostrava, Faculty of Mining and Geology, Ostrava-Poruba, Czech Republic; vladimir.cablik@vsb.cz

Reviewed by Prof. Barbara Tora

The Birac factory is located in the Zvornik industrial area (Karakaj), eastern Bosnia. Located only one kilometre from the Drina river, its red mud waste is conveyed by pipes to the dump area at Đulići, some ten kilometres from the Industry. This waste dump contains at present about ten million tons of red mud and is a big concern of the Industry.

The basic properties of the waste are: very high pH (12.2) of the suspension conveyed to the dump, and extremely fine solids of the suspension. The solids are highly migrative during the slow precipitation and complex in the chemical composition (due to dissolved salts). Red mud is a serious pollutant of the environment both by its chemical composition and the amount generated every year. A part of this waste (cleared water) is conveyed back to the industry and most of the solids remain settled out in the dump.

Red mud is classified for its complex character into the waste unsuitable for treatment and disposal. For many years now researches have been made in the use of this waste and in a safe disposal, neutralization or recultivation of old dumps.

Red mud can be permanently disposed off or used:

— in ceramic industry as an additive to make special ceramics,
— dewatered (ferro-alumina) as a raw material in cement manufacture,
— leached to produce TiO_2,
— in cement industry (Lafarge plants),
— in building material industry as a raw material in manufacture of building and pavement blocks and road surfacing,
— micronized and calcinated as a pigment,
— in agriculture to improve soil quality, spread on the ground to lower the rate of phosphorus leaching by rainwater, etc.

This work also presents a research in the use of red mud as pigment in the building material industry for manufacture of blocks, bricks, and pavement and road surfaces.

1. Aluminium minerals and ores

The principal source of aluminium is bauxite. The ore, first used in 1845 by Dufrenoy, is named after the locality (Les Beaux-de-Provence, near Arles) in France where Pierre Bertier discovered it in 1821. By their mineral composition, the bauxites in ex Yugoslavia, like similar bauxites elsewhere, are dominantly monohydroxide minerals – either boehmite or diaspore. The commonest bauxite minerals that vary depending on the derivation are given in Table 1. Besides the essential minerals, bauxites contain many other elements: Na, K, P, Cr, V, Ga, Zn, Pb, Cu, Ni, etc.

Bauxite ores from ex Yugoslavia are worldwide known for their quality. Potential sources of bauxites are large. The bauxites from Bosnia and Herzegovina (Vlasenica, Bosanska Krupa, Mostar, Kljuc, Krunici, etc.) and Montenegro (Niksic), processed in the Birač Alumina Industry, contain about 55% of Al_2O_3 and about 5% SiO_2.

Until recently, bauxite was believed the only source of aluminium. Some other ores are also used at present to produce aluminium as given in Table 2. The global bauxite reserves are estimated at about 29 million tons (www.gsi.ie/workgsi/mineralas/htm).

TABLE 1

Essential minerals in bauxites

TABELA 1

Podstawowe minerały zawarte w boksycie

Aluminium minerals	
Gipsite	$Al_2O_3 \cdot 3H_2O$
Boehmite	$Al_2O_3 \cdot H_2O$
Diaspore	$Al_2O_3 \cdot H_2O$
Iron minerals	
Hematite	Fe_2O_3
Aluminium hematite	$Al\text{-}Fe_2O_3$
Maghemite	Fe_2O_3
Magnetite	Fe_3O_4
Hydrate hematite	$Fe_2O_3 \cdot H_2O$
Goethite	$HFeO_2$
Aluminium goethite	Al-FeO(OH)
Limonit	$HfeO_2 \cdot H_2O$
Titanium minerals	
Anatase	TiO_2
Rutile	TiO_2
Ilmenite	$FeTiO_2$
Leucoxene	$FeTiO_3$
Silicate minerals	
Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
Quartz	SiO_2

TABLE 2

Unconventional aluminium ores (Jelenković 1999)

TABELA 2

Rudy aluminium (Jelenković 1999)

Ore type	Minerals	Trace elements
Nepheline Group	Nepheline, feldspar, aegirine, alkali amphiboles, etc.	Ga, Rb, Cs, V, Zr
Apatite-nepheline group	Nepheline, apatite, feldspars, amphiboles, aegirine, sodalite, sphene, biotite, magnetite, etc.	Ta, Nb, rare earths
Alunite Group	Alunite, quartz, clay minerals, jarosite, amphoteric silicon oxides, diaspore, etc.	Ba, P, F, V, Ga

The “*Metallurgical bauxite*” is a raw material in the Bayer process for production of alumina – a halfway product to the primary aluminium metal. Although most of the world’s production of bauxite is used for this purpose, large quantities of special ‘non-metallurgical’ grades of bauxite are used in the manufacture of abrasives, refractories, cement and chemicals. Some of these outlets are illustrated in Table 3.

TABLE 3

‘Non metallurgical’ uses of Bauxite* (Discombe 2005)

TABELA 3

„Niemetalurgiczne” wykorzystanie boksytów (Discombe 2005)

Material	Comments
Chemical Grade	Mainly used in water treatment plant chemicals, after conversion of the alumina minerals to aluminium sulphate (low iron gibbsitic bauxites preferred)
High alumina cement	The necessary raw materials differ from Portland cement using for this application a selected quality bauxite plus limestone. Two types generally made *viz*.; high iron product with Al_2O_3:Fe_2O_3 ratio between 2.0 and 2.5:1 and low iron product with Al_2O_3:Fe_2O_3 ratio of 20:1
Portland cement	Only small quantities of bauxite are used to adjust the chemical composition of the cement
Street flux	Viscosity control of slags
Calcined bauxite	Mainly used for refractories and abrasives. Other minor uses are: road surface aggregates; welding flux compositions; as a “proppant” in oil wells, and “activated” bauxite for use as drying agents and absorbents in the petrochemical industries

* www.gsi.ie/workgsi/minerals/newslet/26/26-01.htm

2. Bauxite processing

The Birac Alumina Industry was designed for production of monohydrate bauxite of the average silicate modulus 8.

Bauxite is treated by the Bayer process through the following stages:

1. Bauxite preparation (crushing and grinding).
2. Desiliconization.
3. Leaching.
4. Sedimentation and red mud rinsing.
5. Hydrate dissociation and treatment.
6. Steaming.
7. Calcination.

Milling sizes for bauxite processed in this industry are: on-sieve particles 0.147 mm to 4%, on-sieve particles 0.058 mm to 25%, and particles of ten microns. The final waste of the Bayer process is the bauxite residue – red mud.

Red mud properties. Repeatedly rinsed red mud suspension, of a density between 1.2 and 1.3 g/cm^3 and dry matter concentration from 250 to 350 g/l, is disposed as a waste. The liquid phase of the suspension contains about 7 g/l of Na_2O, a serious pollutant, which is dumped in selected and prepared areas. Red mud from the Birač Industry is dumped in an open field – a natural dump area. The only environmental control work so far has been a reinforced-concrete dam wall.

3. Test sample

A sample of red mud was taken in June 2005 in the Birac Alumina Industry from a transverse cut in the effluent pulp at the ultimate thickener.

During the sample treatment in laboratory, the suspension was left to sediment and then the liquid phase was decanted and the solid phase dried forty hours at the temperature of 105°C. Secondary, representative samples were separated from the dewatered residue and further tested for characterization of the waste material (Fig. 1). Samples were taken for determination of the chemical and mineral compositions, density, grain sizes, calcination and other tests. A portion of the sample was laboratory-dried for two months to study changes in the sample. The average density of the representative dry red mud sample was 3.05 g/cm^3.

a. b. c.

Fig. 1. Visual appearance of the autoclaved red mud after being dried, pulverized and calcinated

Rys. 1. Widok próbek czerwonych mułów po wysuszeniu (a), rozdrobnieniu (b), kalcynacji (c)

4. Analytical methods

Chemical composition was analyzed in the central laboratory of the Birac Alumina Industry, Zvornik. Red mud as a complex multiphase waste was short analyzed on the following compounds: Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, $Na_{2\ tot}$, P_2O_5, V_2O_5, ZnO, MgO, MnO, K_2O, and loss of ignition. Chemical analysis is given in Table 4.

TABLE 4

Chemical composition of red mud

TABELA 4

Skład chemiczny czerwonych mułów

Compound	Rate [%]
Al_2O_3	14.14
SiO_2	11.53
Fe_2O_3	48.50
TiO_2	5.42
CaO	3.96
Na_2O_{uk}	7.50
P_2O_5	0.297
V_2O_5	0.116
ZnO	0.027
MgO	0.049
MnO	0.17
K_2O	0.058
L.O.I.	7.25

The above chemical analysis of the Birac Alumina Industry red mud indicates an expected high percent of compound Fe_2O_3 (48.5%) and high silica (11.53%) and Al_2O_3 (14.14%). The high loss of Al_2O_3 through the bauxite processing suggests inadequate mineral liberation in milling (grind fineness). Of rare metals, notable was the presence of TiO_2 (5.42%), whereas vanadium was much lower (0.116%). Rare metals seldom occur as native minerals in bauxites. They are dispersed in the essential metal structure (aluminium, iron or silicon).

The following data may give an idea of the wide ranges of bauxite constituents (Fe_2O_3 30–60%, Al_2O_3 10–20%, SiO_2 3–50%, Na_2O 2–10%, CaO 2–8%, and TiO_2 trace to 10%.

Red mud very rich in iron can be used as an inexpensive pigment for coloured concrete. The red coloration can be enhanced by calcination within the range from 900 to 950°C.

Red mud calcination was conducted at a very high temperature to achieve decomposition and evaporation of certain components. At a temperature between 900 and 950°C, water (of crystallization and of constitution) was driven off; organic matter burnt, and carbon dioxide produced by disintegration ($CaCO_3$ – CaO + CO_2) also was driven off into the atmosphere. Calcination led to the oxidation of iron, manganese and sulphide. The ignition loss varied from 4.93 to 5%.

Mean density of the representative red mud sample from the Birac Industry was 3.05 g/cm^3, and the ignition loss for the temperatures of 900 and 950°C was 4.93 and 5%, respectively. It should be noted that after the calcination and the conversion of the lower into higher oxides, and after decomposition of the carbonates, the red mud sample acquired the characteristic red colour that makes it usable as a pigment.

Mineral composition of the red mud depends on the mineral composition of the source material – bauxite. Bauxite is a multiphase ore that may contain, according to some references, as many as more than hundred minerals. Its essential constituents, however, are the minerals of aluminium, iron, silicon, titanium, calcium, magnesium, etc. The accessory minerals are those of many other elements: Na, K, P, Cr, V, Ga, Zr, Zn, Pb, Cu, Ni, Mn, Co, etc. Depending on the type of mineral deposits, the amounts of the essential and accessory minerals may vary within wide ranges. Not infrequently, the variations are notable within one and the same deposit.

Aluminium is contained in bauxite in the form of hydrous oxides: hydrargillite, boehmite and diaspore, and at lower rates as corundum (Al_2O_3) or various aluminosilicates. Aluminium minerals are naturally concentrated and mixed in ores with many metals and petrogenic minerals.

The most abundant gangue mineral in bauxites is free silica (various forms of crystalline SiO_2 – quartz, quartzite, chalcedony, or amorphous SiO_2 – opal) or bound silicon oxide (in the form of aluminosilicates, commonly kaolinite). Iron in bauxite occurs in various minerals forming the principal waste (red mud) component. Iron minerals are hematite, magnetite, hydrohematite, goethite, limonite. Its principal carbonates are siderite and ankerite; silicate – chamosite; sulphides and sulphates – pyrite, melanterite, boutlerit, jarosite, etc.

Commonest in bauxite are hematite and goethite, and less common are magnetite and limonite. Titanium is almost always found in bauxites, in the form of rutile, anabase or brucite, of which anabase is the commonest. Bound titanium dioxide may be contained in bauxites in the form of sphene, perovskite or ilmenite. Carbonate constituents are calcite, magnesite, dolomite, hydrous magnesite, ankerite, malachite and azurite. The red mud considered in this work is largely depending on chemical and mineral compositions of the mineral ore, grind fineness and effective leaching (decomposition).

5. Testing pigment production from red mud

The idea to use red mud as pigment in the building material industry was based on the extremely fine particles (4% on sieve 0.147 mm, 25% on sieve 0.058 mm and the remaining percentage of about ten microns) and the characteristic red colour.

Dewatered and ground red mud (waste) was preliminary tested for use as pigment in the building material industry. Similar researches were reported by the Building Research Institute (BRI) of Jamaica; Tübitak Marmara Research Center Gebze-Kacaeli, Turkey; Afyon Kocatepo University, Turkey.

For this test, building blocks were made of the standard mixture (crushed limestone Class 3.3+0 mm, cement and water) with the addition of red-mud pigment in various proportions. Before being added, red mud was homogenized and dewatered and then used as a raw material unground or fine-ground. At the feeding point, the water content varied within the range from 9 to 14 wt%, and the red mud content was between 1 and 33%. The cement types used in the test were white cement (CEM 152.5 N) from the Lukavac Cement Plant and Portland cement (PC 42.5 N) from the Titan Cement Plant of Kosjerić. The components were mixed and homogenized and water was gradually added to the desired mixture density. Then the mixture (sample) was poured into a mould, 8.5 × 4.5 × 15.5 cm in size, and manually pressed. The exact proportions of the constituents are given in Table 7.

A number of blocks were tested for compressive strength after 17-14-28 days of rest at the room temperature (18°to 23°C). The compression test was conducted to the JU Standards for the given materials. The tests were carried out in the Laboratory of Mine Material Testing, using AMSLER Zürich press for determination of the mechanical strength. The test data, given in Table 5, indicate satisfactory compressive strengths. Test blocks are shown in Figure 2.

Compressive strengths, given in the table above, vary from 14.83 to 27.77 MPa. Test block 1 has the lowest compressive strength due to the high red mud constituent (100 g) and to its form (unground). Test block 7 has the highest compressive strength due to the lowest red mud constituent (5 g) and its form (ground). In relation to the compressive strength, all tested samples were satisfactory.

TABLE 5

Composition of test blocks

TABELA 5

Skład badanych bloczków

Test block (sample)	Cement	Limestone –3.3+0 mm	Red mud		Water	Compressive strength	Date of manufacture
	wt%	wt%	wt%	Treatment	wt%	MPa	(Total day)
TEST 1*	22.22	44.44	22.22	Unground	11.12	14.83	01.08.05 (80)
TEST 2*	18.18	54.54	18.18	Unground	9.10	17.39	03.08.05 (44)
TEST 4*	19.42	58.25	7.71	Unground	14.56	25.04	26.08.05 (77)
TEST 5	22.83	63.93	4.51	Ground	8.67		30.08.05
TEST 6	22.22	40.00	26.67	Ground	11.11		01.09.05
TEST 7*	**22.22**	65.56	1.11	Ground	**11.11**	27.77	**05.09.05** (41)
TEST 8*	**21.50**	32.26	32.26	Ground	**13.98**	16.25	**06.09.05** (54)
TEST 9	21.50	43.01	21.50	ground + calcinated	13.99		08.09.05
TEST 10*	21.50	38.72	25.81	ground + calcinated	13.98	17.51	09.09.05 (50)

* Compressive strength measured.

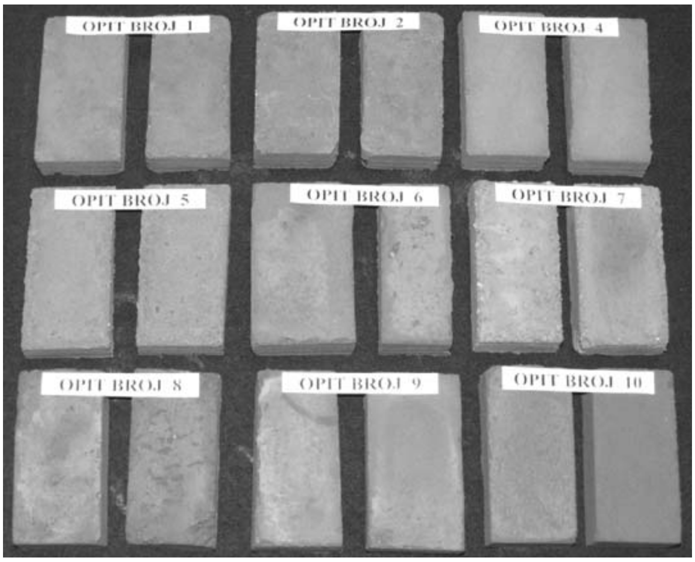

Fig. 2. Comparative shapes of the test blocks. Different colours depend on the amount and preparation of red mud and on mechanical strength

Rys. 2. Porównanie testowanych bloczków betonowych z dodatkiem pigmentu. Kolor zależy od ilości dodawanego pigmentu, sposobu jego przygotowania i wytrzymałości mechanicznej

The preliminary test data approved the usability of red mud (as pigment) in the building material industry, *viz*.: blocks, bricks, pavement surfacing, etc. Of course, for practical application, additional tests will be necessary.

Red mud is a waste generated by the aluminium industry, and its disposal is a major problem for the industry. Very rich in iron, it can be used as a cheap pigment for coloured concrete. The red coloration can be enhanced by calcination within the temperature ranges from 900 to 950°C. The same operation also transforms aluminium hydroxides (goethite and boehmite) and clay minerals into pozzolanic admixtures that are capable to consume the calcium hydroxide produced by cement hydration. Thus, a new admixture – pozzolanic pigment – can be developed for concrete. Pozzolanic properties of calcinated red mud also were studied by monitoring the consumption of different cement and red mud mixtures. A uniform and durable concrete was produced using white cement ground with burnt red mud.

Conclusion

1. Chemical analysis of a red mud sample from the Birac Alumina Industry indicated the following: high Fe_2O_3 (48.50%), much SiO_2 (11.53%) and Al_2O_3 (14.14%). The high percentage of Al_2O_3 suggests inadequate mineral liberation through grinding. Notable constituents were TiO_2 (5.42%) and V_2O_5 (up to 0.116%).

2. Mean density, δ_{mn}, of the red mud was 3.05 g/cm^3. The ignition loss was 4.93% for the temperature of 900°C and 5% for the temperature of 950°C. Red mud acquired the characteristic red colour that makes it usable as a pigment after its calcination and the conversion of lower into higher oxides and after the decomposition of carbonates.
3. Red mud consists of very fine particles (on-sieve size 0.147 mm up to 4%, size 0.058 mm up to 25%, and the prevailing ten microns size class) and has a characteristic red colour, which were the reasons for its testing for use in the industry of building materials as a pigment for standard concrete mixtures.
4. Red mud was added as a pigment in various proportions (dried not ground, ground, calcinated) to concrete mixes of standard test blocks (ground limestone size fraction –3.3+0 mm, cement and water). The test blocks varied in colour depending on the mix and the amount of red mud added. The blocks were tested for compressive strength after having rested 7, 14 or 28 days at the room temperature (18 to 23°C). Compressive strengths from 14.83 to 27.77 MPa of the blocks that contained red mud from 1 to 32% were satisfactory.
5. The started preliminary tests (manufacture of pavement and building blocks and bricks) have shown that red mud, a waste of silica production by the Bayer Process, could be used in the building materials industry as an additive to good products (high compressive strength, characteristic red colour and resistance to atmospheric effects).

While the generation of wastes is daily increasing with the ever faster industrial development and the environmental control is becoming stricter, adequate legal restrictions and greater efforts of scientists are expected in the future.

A "universal" technique of disposal, management and full utilization of red mud, an alumina production waste, has not yet been developed. Characterization of this waste material can determine its uses in different industries or the places and methods of disposal and management that would come close to a technology harmless to the environment.

The reported tests have shown that neutralized, dried, calcinated and ground red mud is usable as pigment in the building materials industry, in the manufacture of pavement surfacing and building blocks, bricks, etc. For these uses, however, additional mechanical tests will be necessary.

REFERENCES

Glanville J.I., 1991 — Bauxite waste bricks (Jamaica): evaluation report. June 1991. IDRC, Ottawa. 16 pp. in various pagings.

Jelenković R., 1999 — Ležišta metaličnih mineralnih sirovina (Deposits of Metallic Minerals). RFG, Beograd.

Jusufbegović Ž., 1990 — Receptura za beton (Formula for Concrete), FSD, Tuzla.

Krgovic M.M., Blagojevic N.Z., Jacimovic Z.K. and Zejak R., 2004 — Possibilities of using Red Mud as Raw Materials Mixture Component for Production of Bricks. Research Journal Of Chemistry And Environment. Volume 8, No. (4).

Majstorović M., 1978 — Opšta tehnologija u proizvodnji glinice sa tehnologijama zanimanja proizvodnih odelenja (Fundamental Technology in Alumina Production and Technologies of Production Plants). Rudarski institut, Sarajevo.

Medvedev M., Siziakov V.M., 1986 — Hidrogranatni postupak prerade visokosilicijske boksitne sirovine alternativa za Bajerov proces (Hydrogarnet Treatment Technique for Silica-High Bauxite – a Bayer Process Alternative). Leningrad Institute (LOZ VAMI).

Nikolić M., 2001 — Ispitivanje rude boksita ležišta "Krunići" – Srebrenica, diplomski rad (Testing Bauxite Ore from Krunići Deposit at Srebrenica, graduation thesis). RGF, Beograd.

Rezultati analize centralne laboratorije fabrike glinice "BIRAČ" (Birač Alumina Industry Central Laboratory Report). FSD Birač.

Tomanec R., 2000 — Metode ispitivanja mineralnih sirovina u pripremi mineralnih sirovina (Mineral Examination Methods in Mineral Processing). RGF, Beograd, pp.315.

Pera J., Boumaza R. and Ambroise J., 1997 — Development of Pozzolanic Elsevier Science Ltd. Pigment from Red Mud. Cement and Concrete Research, vol. 27, no. 10, pp. 1513–1522.

Vračar R., Živković Ž., 1993 — Ekstraktivna metalurgija aluminijuma (Aluminium Extractive Metallurgy). TMF, Beograd.

Web sites

www.gsi.ie/workgsi/minerals/newslet/26/26-01.htm
www.gsi.ie/workgsi/mineralas/htm
www.euromines.org
www.world-aluminium.org/environment/challenges/rehabilitation.html
www.mic-d.com/gallery/darkfield/bauxiterocklow.html
www.metallicaminerals.com.au/aluminium_bauxite_projects.htm
www.world-aluminium.org/environment/challenges/residue.html
www.azom.com/details.asp?ArticleID=2071#_The_Bayer_Process
www.environment.about.com
www.edugreen.teri.res.in
www.indiaone.com
www.unesco.org
www.unep.org
ww.unfpa.org
www.epa.org
www.mona.uwi.edu/uwihome.html
www.world-aluminium.org/environment/challenges/rehabilitation.html
www.metallicaminerals.com.au/aluminium_bauxit...

VLADIMIR CABLIK

CHARAKTERSYTYKA I ZASTOSOWANIE CZERWONYCH MUŁÓW Z PROCESU PRZETWÓRSTWA BOKSYTU

Słowa kluczowe

Czerwone muły, pigment, boksyt

Streszczenie

W artykule przedstawiono charakterystykę czerwonego mułu – odpadów powstających w procesie produkcji aluminium metodą Bayera. Przeprowadzono analizę pozostałości po przeróbce boksytów w celu określenia ich składu mineralogicznego, określono również skład chemiczny, skład ziarnowy oraz gęstość produktu. Produkt został poddany kalcynacji, a następnie została zbadana jego przydatność jako czerwonego pigmentu dla barwienia wyrobów przemysłu budowlanego. Badaniu poddano kostki betonowe wytworzone z dodatkiem pigmentu, określając ich wytrzymałość po 7, 14, i 28 dniach w temperaturze pokojowej.

Uzyskany pigment charakteryzuje się następującym składem chemicznym: Fe_2O_3 – 48,50%, SiO_2 – 11,53% oraz Al_2O_3 – 14,14%. Średnia gęstość czerwonych mułów wynosiła 3,05 g/cm^3. Straty prażenia 4,93% dla temperatury 900°C i 5% dla temperatury 950°C. Czerwone muły uzyskują kolor w wyniku procesu kalcynacji. Pigment charakteryzuje się drobnym uziarnieniem – zawartość klasy powyżej 0,147 mm – 4%. Pigment był dodawany do standardowego betonu (o składzie: kruszywo, cement i woda) w ilości od 1 do 32%.