Strength of Hydrated Cement Based on Borogypsum

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Abstract. The paper presents research into the strength of hydrated cement based on borogypsum.

1. Introduction

Russia’s economic potential is largely dependent on its mineral reserves. Minerals are non-renewable and scarce; the current extensive production and processing strategy exacerbates the problems pertaining to the rational use of such materials [1]. Recycling industrial waste is a promising solution that helps save resources and environment. As numerous mining and metallurgical enterprises deplete their fields, man-made facilities may turn into a high-priority source of minerals, if not the only one [2].

In the Far East, years of mining and chemical production produced millions of tons of anthropogenic waste, which is currently left unrecycled. This includes boric acid production waste (borogypsum), dozens of millions tons of which has been accumulated at the Bor facility in Dalnegorsk, Primorsky Krai, as well as at the Komsomolsk Sulfuric Acid Factory. This is an environmental disaster for Komsomolsk-on-Amur, where the sulfuric acid factory used to be. The factory grounds still contain a sludge tank that contains borogypsum; as it is collapsing, boron infiltrates into groundwater [3]. The Long-Term Plan for Comprehensive Socioeconomic Development of Komsomolsk-on-Amur was approved in 2016; this plan calls for designing and taking action to address the environmental hazard represented by the sludge tank; the plan provides funding to that end. The Ministry of Natural Resources of the Russian Federation has developed the Roadmap for Designing and Taking Measures to Handle the Environmental Hazard Represented by the Borogypsum Leaking from the Sludge Tank of the Former Komsomolsk Sulfuric Acid Factory [4, 5].

Virtually no systematic research on integrated borogypsum recycling has been done since the early 1990s.

In the 1970s, the Bor facility launched a borogypsum recycling plant to test a process for thermal decomposition of such waste to produce sulfurous gas and carbon monoxide. The plant was designed to further design a pilot shop to recycle borogypsum and produce sulfuric acid and cement [6]. In the 1980s [7], they proposed a technology to recycle borogypsum to produce wollastonite and sulfur
dioxide. Some papers propose producing calcium sulfate dihydrate, silicon dioxide, and liquid sodium glass from borogypsum [8–10].

Proposals were made in various years, to use borogypsum to make construction materials. Boric acid production waste (borogypsum) is different from phosphogypsum or fluorogypsum chemically and mineralogically in that it has approximately equal molar proportions of calcium sulfate dihydrate and X-ray amorphous silica, which interacts with calcium hydroxide released when hydrating Ca$_3$SiO$_5$, which also produces silicates that positively affect the strength of hydrated cement.

The goal hereof is to study how borogypsum found at the Bor facility in Dalnegorsk, Primorsky Krai, can affect the strength of hydrated cement.

2. Experimentation

Source materials used in this research included clinker produced by the Spassky Cement Factory (SCF, М500ДО), natural gypsum produced in China (APA-21), and borogypsum. The natural Chinese gypsum (APA-21) that the SCF uses to make cement contains 52.5% of CaSO$_4$·2H$_2$O, which means its SO$_3$ content is 24.7 wt%.

The phases of these substances were studied by X-ray diffractometry (XRD): CuKα, Ni filter, mean wavelength $\lambda = 1.5418$ Å, imaging angle range 0°–80°, scanning step 0.02°, spectra sampling rate 5°/min. The diffractometer in use was a D8 Advance unit by Bruker, Germany.

X-ray fluorescence (XRF) was applied to borogypsum waste using an S4 Pioneer XRF spectrometer by Bruker AXS, Germany. Relative measurement error was ±2%.

Specific surface was found by low-temperature nitrogen absorption using a Sorbtomer-M unit, Russia.

Gamma spectrometry for natural radionuclides $^{40}$K, $^{226}$Ra, $^{232}$Th was performed using GammaPlus a scintillation gamma spectrometer by Aspect, Russia.

Thermogravimetric analysis (TGA) was performed on a Q-1000D Paulik/Paulik/Erdei derivatograph made by MOM, Hungary; tests were done in an open platinum crucible in the air. Temperature measurement accuracy was ±5°C.

Cement was produced by co-grinding clinker and borogypsum (pre-dried to a constant weight at 50±5°C) or natural gypsum at 2.8 wt% SO$_3$, which corresponded to 130 g of natural gypsum or 98 g of borogypsum per kg of clinker. Clinker and gypsum were co-ground after being preliminarly crushed in a ЩД-6 crusher to reduce the particle size to 2–20 mm. After mixing clinker and gypsum, cement was ground using an МЛ-40 ball mill that further reduced the particle size to 74 μm. The degree of grinding was determined by measuring the particles that didn’t pass a #008 sieve, as well as by the specific surface as measured by a T-3 air passer. Loss of cement with dust was measured as well.

Unsieved residue, МЛ-40 mill: clinker + natural gypsum (APA-21); as well as that of the clinker-borogypsum combination was determined by using a ball as a load. 40-mm balls weighed 6.7 kg, while the clinkers were optimized for 3.5 kg. Grinding time was 7 hours regardless of the cement; 8% of the material was retained by the sieve, while the specific surface totaled 4,000 and 4,250 (±150 cm$^2$/g) for cement that uses natural gypsum and borogypsum.

The two prepared batches of cement were sieved through a #009 sieve before use. To make cement dough, all components were exposed to room temperature. Single-sized Volsky sand (GOST 6139-2003) was used to make the cement dough. 1,350 grams of sand and 450 grams of cement was used per mixing. Normal cement dough density (22.25%) and curing time were found: curing began in 160 to 170 minutes and ended in 200 minutes. Volume was measured to assess the uniformity of its change after boiling the cement pats for three hours. Specimens passed the tests and met GOST 310.3-76 requirements.

The uniformity of particle distribution in the specimens (compressed tablets) of borogypsum-based cement was assessed by analyzing the intensity of characteristic X-ray emitted by the elements when tested by a JXA-8100 (Japan) electron-probe microanalyzer at an accelerating voltage of 20 kV.

The specimens were tested for elements by energy dispersive X-ray fluorescence spectrometry using a Shimadzu EDX 800 HS unit, Japan.
Cement bars were tested for compressive and flexural strength per GOST 310.4-81 indoors at 20±2°C and a relative humidity of at least 50%. Potable water was used to make and store the specimens; the vessels and molds were made of steel. The consistency of the mortar was assessed before testing. To consolidate the mortar, the bar mold and its nozzle were fastened on a vibrating platform. After exposure to vibration, the mold and the specimens it contained were placed in a humidity chamber with a hydrolock that sustained a minimum humidity of 90%. After 24-hour exposure, the specimens were extracted from the chamber and from their molds, then placed horizontally in a bath of potable water.

After testing the specimens for strength (Exposure Day 28), some of the material was ground to particles sized 5 to 6 mm, then analyzed using an ASAP 2020MP unit by Micromeritics, USA.

3. Results and Discussion

3.1. Borogypsum Description
Decomposing the datolite concentrate with sulfuric acid produces solid waste that contains 0.9 to 2.2 wt% of B₂O₃, hence its name “borogypsum”. Borogypsum mainly contains calcium sulfate dihydrate and amorphous silica. X-ray of a borogypsum specimen (Figure 1) dried at 50 to 55°C matched that of a gypsum dihydrate, monoclinic modification, with the following lattice parameters: a = 5.67900; b = 15.20200; c = 6.52200; α = 90.000; β = 118.430; γ = 90.000.

Borogypsum has the following primary components, wt%: SiO₂ – 26–28; CaO – 26–28; SO₄²⁻ – 38–40; Fe₂O₃ – 1.8–2; Al₂O₃ – 0.6–0.8; B₂O₃ – 0.7–1.2; MnO – 0.2; MgO – 0.1–0.2.

Specific surface of borogypsum found by multipoint low-temperature nitrogen absorption is ~22.1 m²/g, while the Greg-Sing comparative method returns ~16.8 m²/h.

![Diffractogram of borogypsum](image)

**Figure 1.** Boric acid production waste (borogypsum): diffractogram.

Gamma spectrometry produced estimates of effective specific radioactivity of natural nuclides (⁴⁰K, ²²⁶Ra, ²³²-Th), which was 17.9 Bq/kg of borogypsum waste, meaning the material could be used as construction material per GOST 30108-94 [16, 17].

Borogypsum TGA showed (Figure 2) that the sample lost 12.6% of its weight. Adsorbed water was lost at 36 to 105°C; the loss amounted to 1.2%, which causes an appropriate endoeffect. At 107 to
122°C, gypsum was gradually dehydrated, which caused two narrow endoeffects that triggered water molecule removal peaking at 140 and 165°C; weight loss totaled 11.4% (dry matter).

Figure 2. Borogypsum TGA.

3.2. Strength of Hydrated Cement
Figure 3 shows the distribution of elements in cement specimens (compressed tablets) made of borogypsum. No difference detected in the element distribution.
Quantitative element analysis based on energy dispersive spectrometry identified the following elements in the borogypsum-based cement (carbon excluded), wt%: 41.7 O; 1.92 Al; 6.93 Si; 2.02 S; 0.62 K; 1.54 Fe; 32.4 Ca; 0.22 Na; and 0.58 Mg.

XRD identified tricalcium silicate, dicalcium silicate, and traces of calcium sulfate dihydrate.

Figure 4 shows the flexural and compressive of cement bars as a function of exposure time. As shown in Figure 4, replacing natural gypsum with borogypsum improved the compressive and flexural strength of hydrated cement by up to 18% on Day 28. Greater flexural strength indicated better resistance to cracking.
Figure 4. Compressive (A) and flexural (B) strength of hydrated cement as a function of exposure time.

Figure 5. Nitrogen absorption and desorption isotherms.
After testing the specimens on Day 28 for strength and grinding some of the material to particles sized 5 to 6 mm, ASAP 2020MP was used to obtain nitrogen absorption and desorption isotherms, see Figure 5. As shown in Figure 5, the borogypsum specimen had 10 to 13 percent higher absorption capacity at relative pressure levels near 1. The studied material is a transient porous body with pores up to 10 nm in diameter; it has a capillary-condensational hysteresis loop.

4. Conclusions

Thus, studies have shown that replacing natural gypsum with boric acid production waste (collected from the Bor facility, Dalnegorsk, Primorsky Krai) does improve the compressive and flexural strength of hydrated cement by up to 18% on Day 28. Creating a production line to use borogypsum to make additives for construction will improve the economy, social situation, and the environment in the locations of sludge tanks, as the approach helps expand the product range, create new jobs, and recycle bulk man-made waste.

References

[1] Evdakov L N, Vorobyev A V 2014 Methodological basis of economic assessment of waste use in clothing Manager 3(49) pp 42-45
[2] Komarov M A, Aliskerov V A, Kusevich V I, Zavertkin V L 2007 Mining-industrial waste - an additional source of mineral raw materials Mineral resources of Russia. Economics and management 4 http://www.vipstd.ru/gim/content/view/407/197/
[3] The next ecological PE is recorded in Komsomolsk-on-Amur http://www.ecoindustry.ru/NEWS/view/36663.html
[4] Long-term plan of comprehensive socio-economic development of Komsomolska-on-Amur http://2032.kmscity.ru.
[5] Protocol of public discussions on the object of eco-examination of the draft territorial scheme in the field of waste management https://www.kmscity.ru/activity/environment/protokol-expert.html.
[6] Krasnikov I S 1999 BOR: the flagship of mining chemistry of Primorye - 40 years (Khabarovsk: Publishing House "Priamursky Gazette") 176 p
[7] Ershov V A, Yumashev L V, Kuznetsov V L, Yegorov A A, Stepanov E V A p 1446129 А1 USSR, C 04 V 35/22 Method of producing synthetic wollastonite and sulphur dioxide № 4249093/31-33 25.05.87 23.12.88 Bul No 47
[8] Semlev V S, Reutov V A, Condrikov N B Stalemate 2324654 Russian Federation IASC C01F 11/46 B03D 1/02 Method of processing gypsum-containing raw materials № 2006127319/15 27.07.2005 20.05.08 Bul No 14
[9] Kindalyuk E G, Semlyov V S, Condrikov N B, Reutov V A 2007 Leaching of borogypsum slimes Chemistry and chemical formation: IV Intl. Symposium May 16-19, 2007 Vladivostok: nauch. Tr. (Vladivostok) p 182
[10] Semlyov V S, Kindalyuk E G, French D A, Condrikov N B, Reutov V A 2007 Production of liquid sodium glass Chemistry and chemical formation: IV Intl. Symposium Vladivostok: nauch. Tr. (Vladivostok) pp 196-197
[11] Vescheryakov Yu G 1982 Gypsum associated industrial products and their use in the production of construction materials (L.: Stroyizdat, Leningrad branch) 144 p
[12] Dymsky V M, Shevyakov T S Stalemate 2036178 Russian Federation IASC C04B11/02 Production method of gypsum binder № 4841147/33 29.05.1990 27.05.1995
[13] Projects implemented by KnAGTU Technopark http://techzonekms.ru/projects.html
[14] Grigoryan K G, Baginova L G, Ayrapetyan S M, Khachatryan A A, Harutyunyan G A, Aznauryan A N, Grigoryan O V 2016 Binding material based on borogypsum Chemical technology 2 pp 50-54
[15] Grigoryan K G, Baginova L G, Hayrapetyan S M, Hachatryan A A, Arutyunyan G A, Aznauryan A N, Grigoryan O V 2016 The knitting material on the basis of a borogips the
Scientific and practical conference with the international participation "Social and economic development of monotowns: traditions and innovations" (Vladivostok: DVFU) pp 67-69

[16] Gordienko P S, Jarusova S B, Kolzunov V A, Sushkov Yu V, Tereznickenko A I, Krysenko G F, Barinov N N 2011 Production of calcium silicates from wastes of boron-containing mineral raw materials processing *Chemical technology* 3 T 12 pp 142 – 147

[17] Yarusova S B, Gordienko P S 2014 Complex Processing of Boric Acid Production Wastes *Materials of the International Meeting "Progressive Methods of Enrichment and Complex Processing of Natural and Man-made Minerals"* (Plaksin Readings - 2014) Almaty (Republic of Kazakhstan) (Karaganda: Arco lIL) pp 381-384