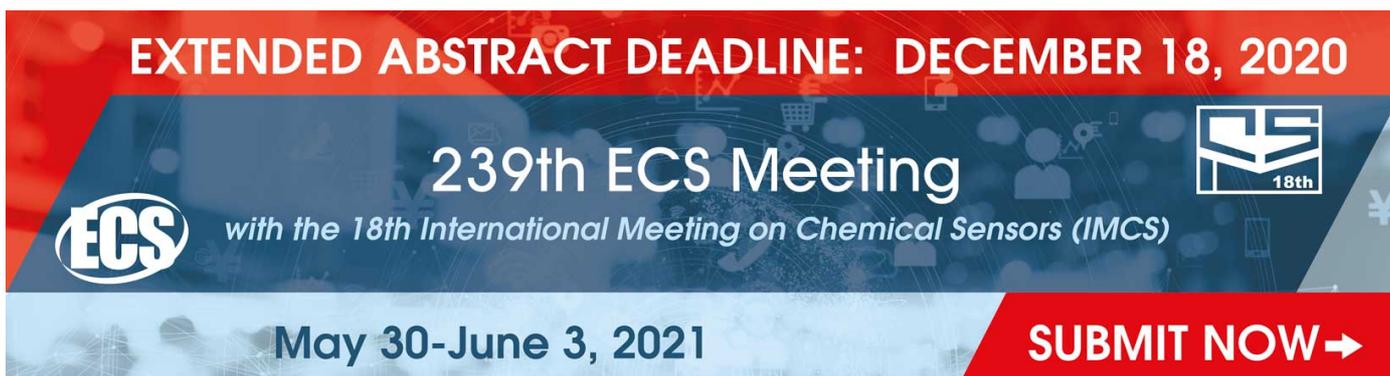


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To cite this article: P S Gordiyenko *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **753** 022002

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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_3SiO_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, M500ДO), 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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which means its SO_3 content is 24.7 wt%.

The phases of these substances were studied by X-ray diffractometry (XRD): $\text{CuK}\alpha$, Ni filter, mean wavelength $\lambda = 1.5418 \text{ \AA}$, imaging angle range $0\text{--}80^\circ$, scanning step 0.02° , spectra sampling rate $5^\circ/\text{min}$. 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 $\pm 2\%$.

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 $\pm 5^\circ\text{C}$.

Cement was produced by co-grinding clinker and borogypsum (pre-dried to a constant weight at $50 \pm 5^\circ\text{C}$) 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 preliminarily crushed in a ШЦЛ-6 crusher to reduce the particle size to 2–20 mm. After mixing clinker and gypsum, cement was ground using an MJL-40 ball mill that further reduced the particle size to $74 \mu\text{m}$. 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, MJL-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 ($\pm 150 \text{ cm}^2/\text{g}$) 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 $20 \pm 2^\circ\text{C}$ 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 soild waste that contains 0.9 to 2.2 wt% of B_2O_3 , 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: $a = 5.67900$; $b = 15.20200$; $c = 6.52200$; $\alpha = 90.000$; $\beta = 118.430$; $\gamma = 90.000$.

Borogypsum has the following primary components, wt%: SiO_2 – 26–28; CaO – 26–28; SO_4^{2-} – 38–40; Fe_2O_3 – 1.8–2; Al_2O_3 – 0.6–0.8; B_2O_3 – 0.7–1.2; MnO – 0.2; MgO – 0.1–0.2.

Specific surface of borogypsum found by multipoint low-temperature nitrogen absorption is $\sim 22.1 \text{ m}^2/\text{g}$, while the Greg-Sing comparative method returns $\sim 16.8 \text{ m}^2/\text{h}$.

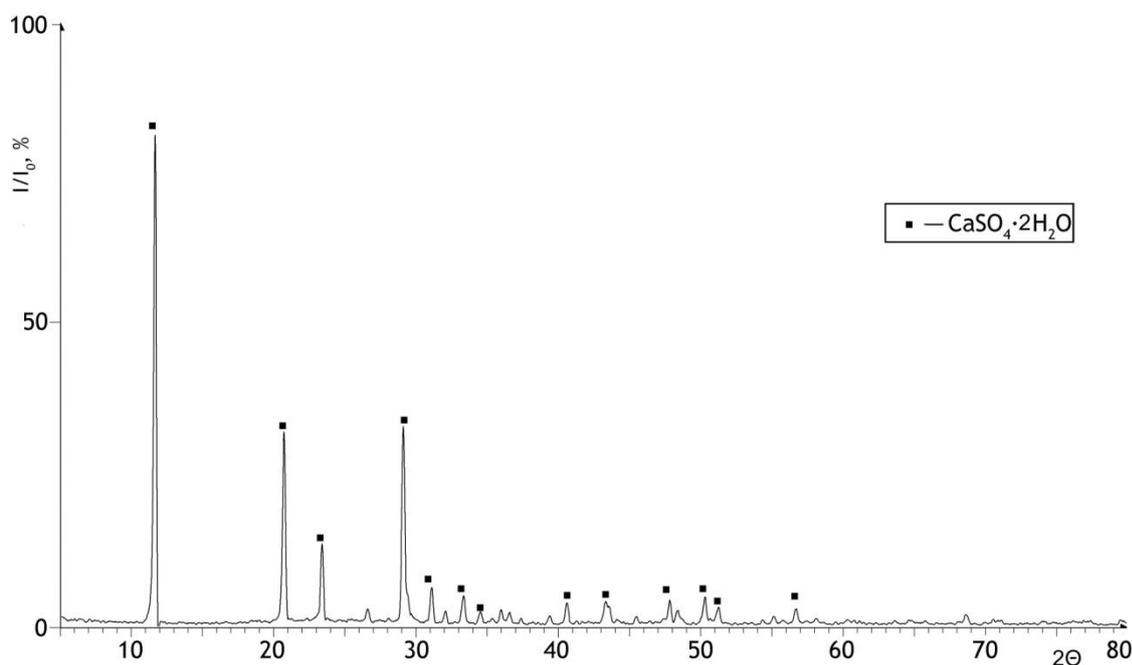


Figure 1. Boric acid production waste (borogypsum): diffractogram.

Gamma spectrometry produced estimates of effective specific radioactivity of natural nuclides (^{40}K , ^{226}Ra , ^{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 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).

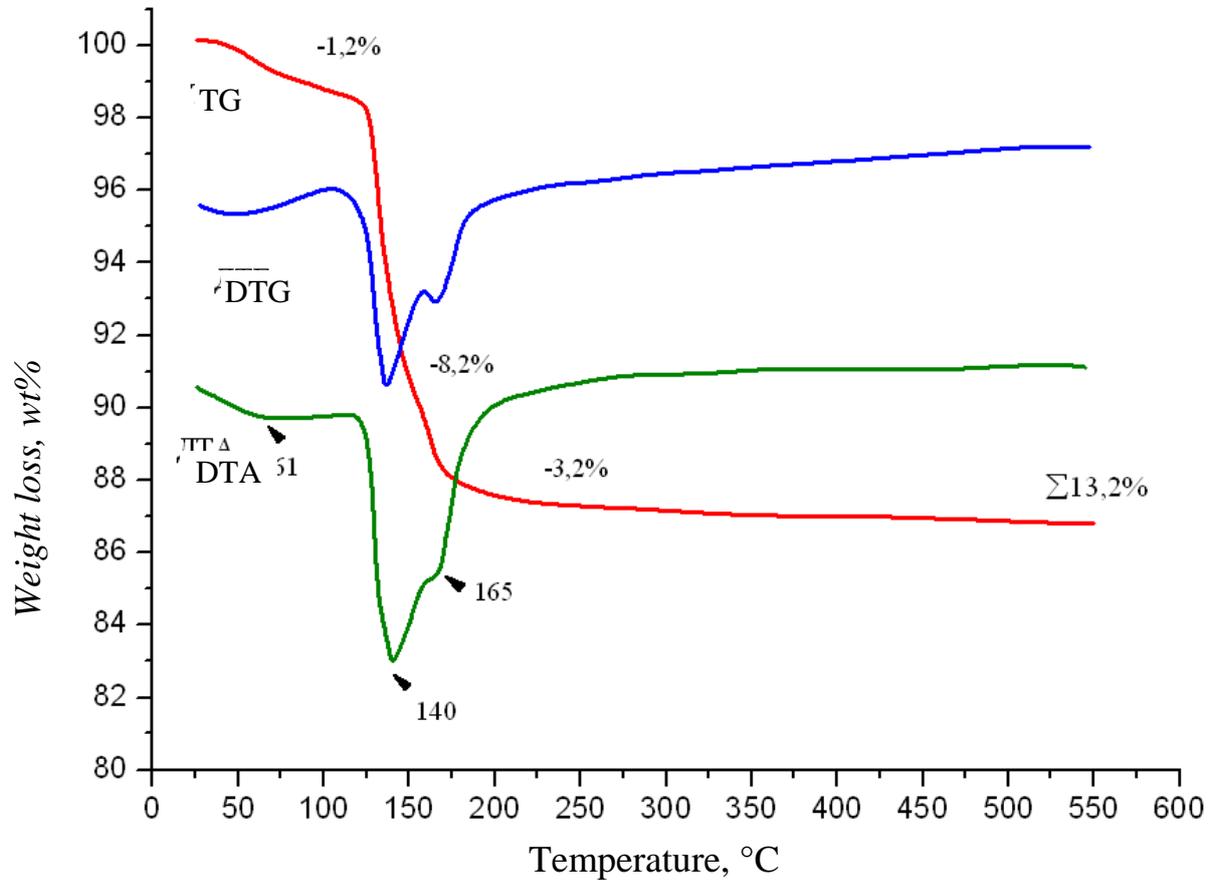


Figure 2. Borogypsum TGA.

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.

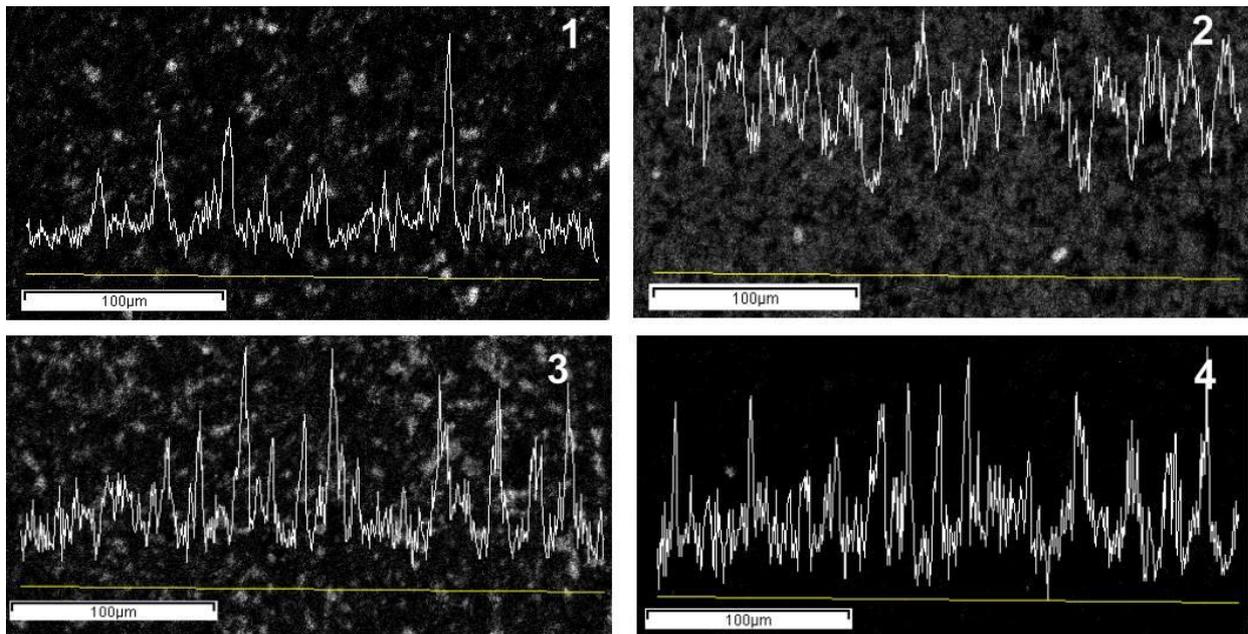
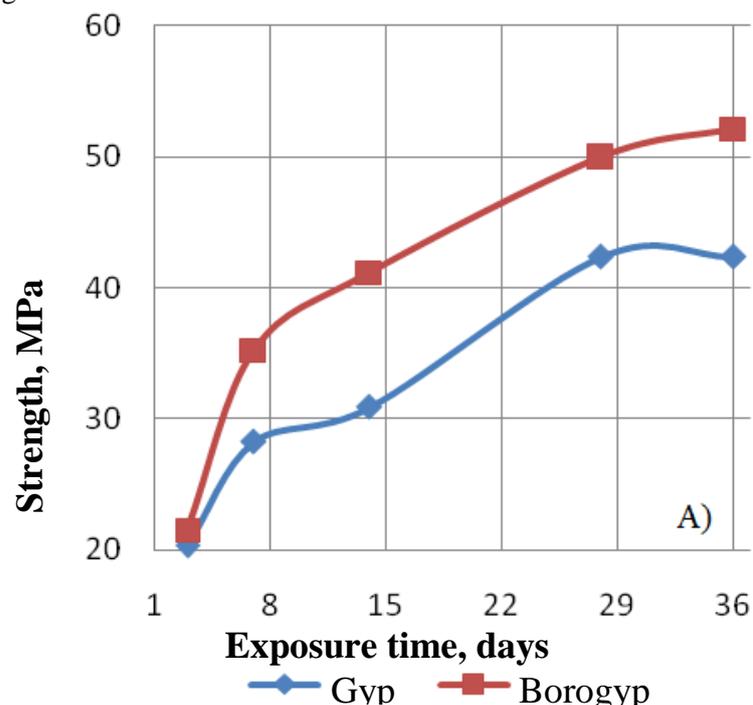


Figure 3. Distribution of elements in compressed cement: 1 for sulfur; 2 for silicon; 3 for aluminum; 4 for iron.

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.



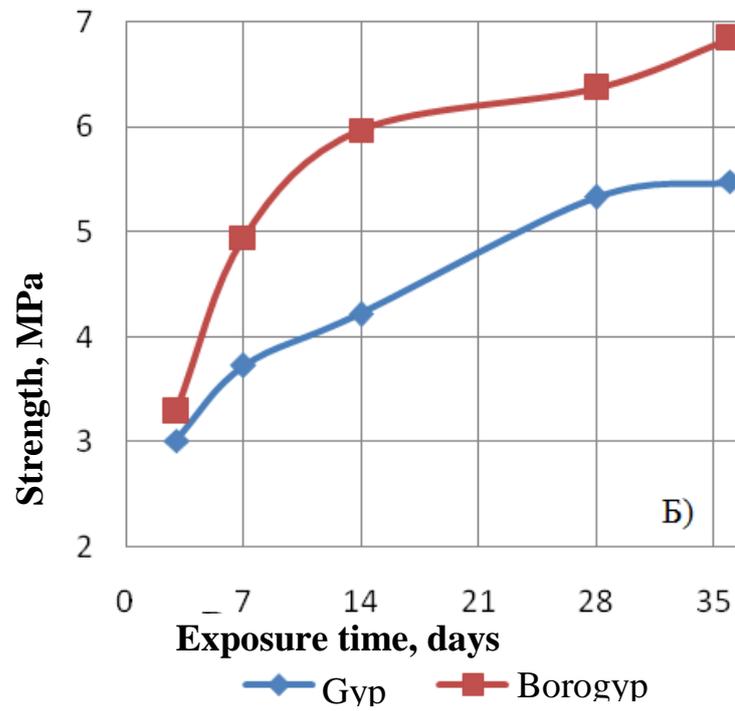


Figure 4. Compressive (A) and flexural (B) strength of hydrated cement as a function of exposure time.

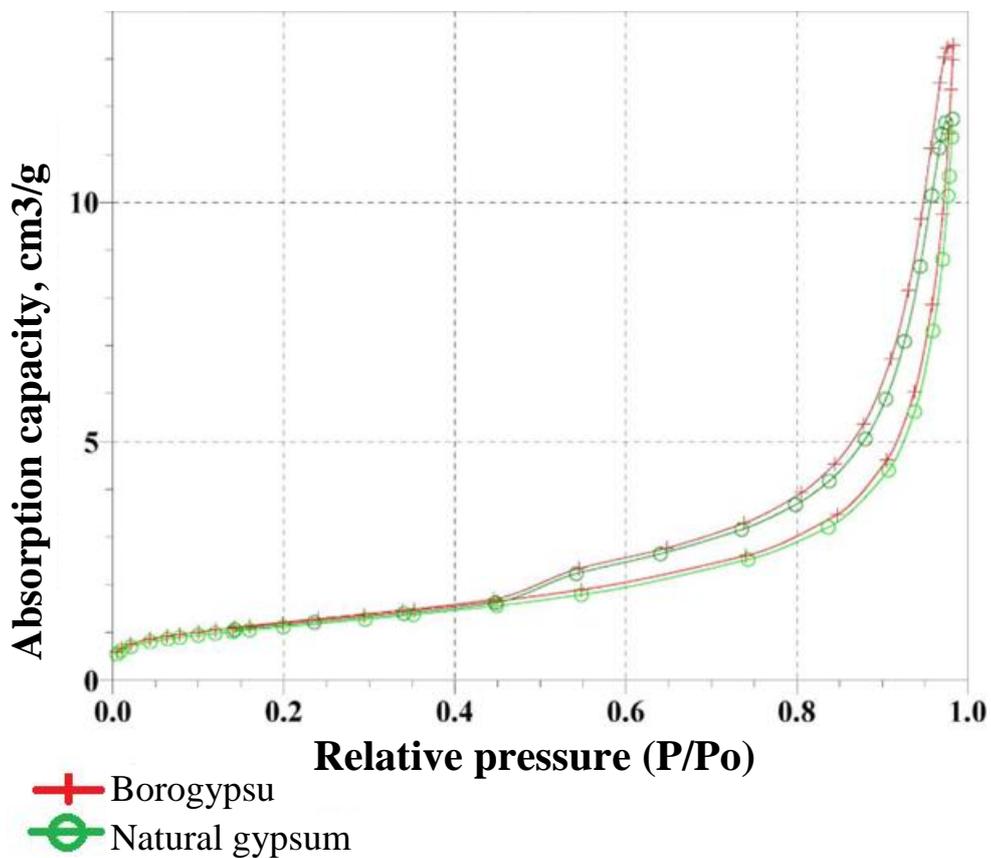


Figure 5. Nitrogen adsorption and desorption isotherms.

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.

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