Issue VII, November 2024
e-ISSN 2707-9481 Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan
ISBN 978-601-80473-3-6 https://doi.org/10.31643/2021.06

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The use of diatomites in industrial production technologies

Abstract: General information on the distribution and reserves of diatomites in the world and Kazakhstan is presented, and their physical and chemical properties and applications are described. Diatomites have several valuable properties: high porosity, refractoriness, acid resistance, low thermal and acoustic conductivity, low bulk density and due to the large specific surface exhibit significant absorption capacity. It allows them to be used as fillers and heat-insulating materials in building technologies, filtering materials in the food industry, adsorbents in medicine, soil structuring agents, and carriers of insecticides in the agricultural sector. The technologies for obtaining several industrial products using Kazakhstani diatomites are described: as dry building mixtures, silicate bricks, foam glass, hydraulic binders, and iron oxide pigments.

Keywords: diatomites, industrial application, dry building mixtures, foam glass, iron oxide pigments.

Introduction

Distribution, reserves and industrial applications of diatomites in the world

World diatomite reserves are more than 1 billion tonnes, of which about 250 million tonnes are attributable to the United States and 110 million tonnes to China, as estimated by the US Department of the Interior (USGS) Geological Survey (Kuldeyev et al., 2020).

The volume of diatomite production worldwide is over 2.5 million tonnes per year. According to the USGS, the bulk of diatomite is produced in the USA (0.9 million tonnes - 36 % of global production), China (16 %), Denmark (12 %), Japan (6 %), Mexico (6 %) and France (3 %). The USA is the largest producer, consumer and exporter of diatomite. The CIS accounts for 4 % of the world's diatomite production (Ospanov et al., 2022).

The diatomite market in the USA is estimated at an average annual value of 180 million USD. The USA is the world's leading producer and consumer of diatomite. The main applications of diatomite in the USA are filtration - 67 %, use as cement additives - 15 %, adsorbent - 11 %, filler - 7 %, other areas, including the production of specialised pharmaceutical products - less than 1 % (Kuldeyev et al., 2020).

Diatomite is mainly used in filtration products to purify beer, spirits and wine, as well as fats and oils. It is also used in the production of absorbents, fillers, lightweight aggregates and other applications. Diatomite is used to remove microbial contaminants (e.g., bacteria, protozoa and viruses) in municipal water supply systems. Small amounts (less than 1 %) are used in specialised pharmaceutical and biomedical applications: in human blood plasma filtration, pharmaceutical processing and as a non-toxic insecticide

(Yurkov & Aksel'rod, 2005; Yıldız; 2008; Akhtar et al., 2009; Ediz et al., 2010; Flower, 2013; Ha et al., 2013; Matsunaga et al., 2017; Ahmadi et al., 2018; Nakashima et al., 2021, Kenzhaliyev et al., 2021).

The unit cost of diatomite in the US market varied widely in 2019, ranging from around $10 per tonne when used as a lightweight aggregate in Portland cement concrete to over $1,000 per tonne in specialised applications such as cosmetics, DNA extraction and others.

Diatomite is a finely dispersed sedimentary rock and is a type of siliceous (opal-cristobalite) raw material. Siliceous raw materials also include sedimentary rocks similar to diatomite in genesis and composition: opokas and trepels. Diatomite consists mainly of silica (80-90 %), aluminium and iron oxides. In diatomites, silica is represented mainly by the smallest shells of diatom algae (diatoms), the number of which in the rock can reach 10-20 million/cm^3. About 10 thousand different species of diatoms are known. Opokas have higher strength, and silica in them is represented by the smallest (less than 0.005 mm) globular and micrograined particles. Trepels resemble diatomites in appearance and opokas in microstructure.

Diatomite is a type of siliceous raw material with high porosity, poor thermal and acoustic conductivity, refractoriness and acid resistance. Diatomite is relatively inert and has high absorption capacity, large surface area and low bulk density. Due to their specific properties, diatomites are considered as multipurpose mineral raw materials and are used in various industries (see Figure 1 by Flower, 2013).

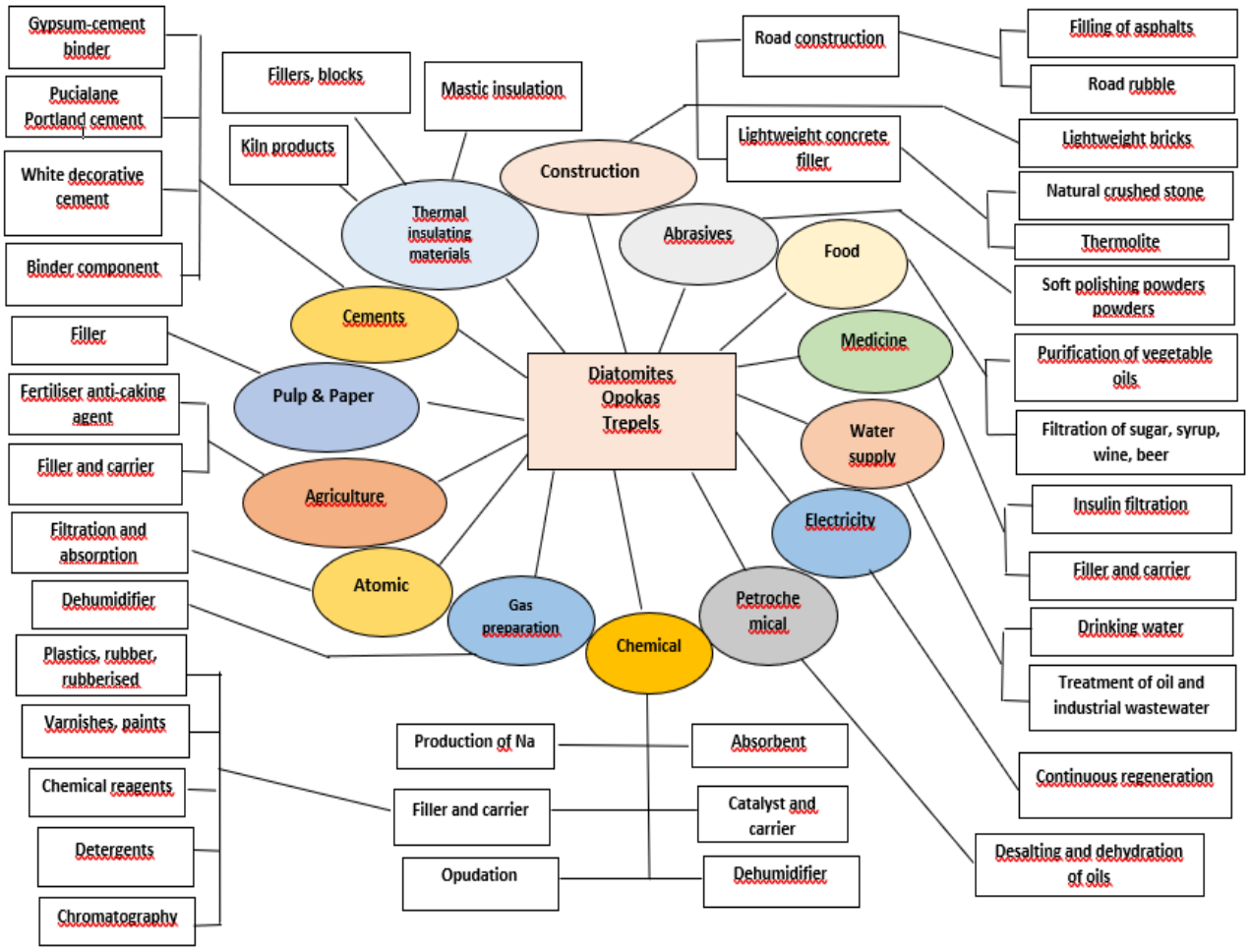

Figure 1. Applications of siliceous minerals (Flower, 2013)

Research Methods

The following methods of analysis were used to establish the composition of the initial raw materials and the obtained products: mineralogical, chemical, X-ray phase, X-ray fluorescence, electron scanning microscopy. Equipment: atomic emission spectrometer Optima 2000 DV; X-ray diffractometer D8 Advance

BRUKER, Cu α-radiation; X-ray fluorescence spectrometer Venus 200 PANalytical B.V.; electron probe microanalyser JXA-8230 (JEOL), Tamman furnace.

Research Results

Distribution, reserves and physical and chemical characteristics of diatomites from Kazakhstan

Kazakhstan has large reserves of diatomite raw materials (more than 200 million tonnes), which are concentrated in the Aktobe region and are currently involved in industrial processing on a small scale (https://avestnik.kz/diatomit-universalnyiy-i-unikalnyiy/). The main physical, chemical and mechanical characteristics of natural diatomites of the Zhalpak deposit have been studied. Samples of diatomite raw materials are characterized by a significant variation in chemical composition. SiO_2 content varies from 73.11 % in white varieties of raw materials to 25.87 % in yellow (ochre-like) ones. The Fe_2O_3 content varies from 2.36 % to 30.42 %. Sodium, potassium, magnesium, calcium, barium and aluminium silicates are also present in insignificant amounts (Figure 2).

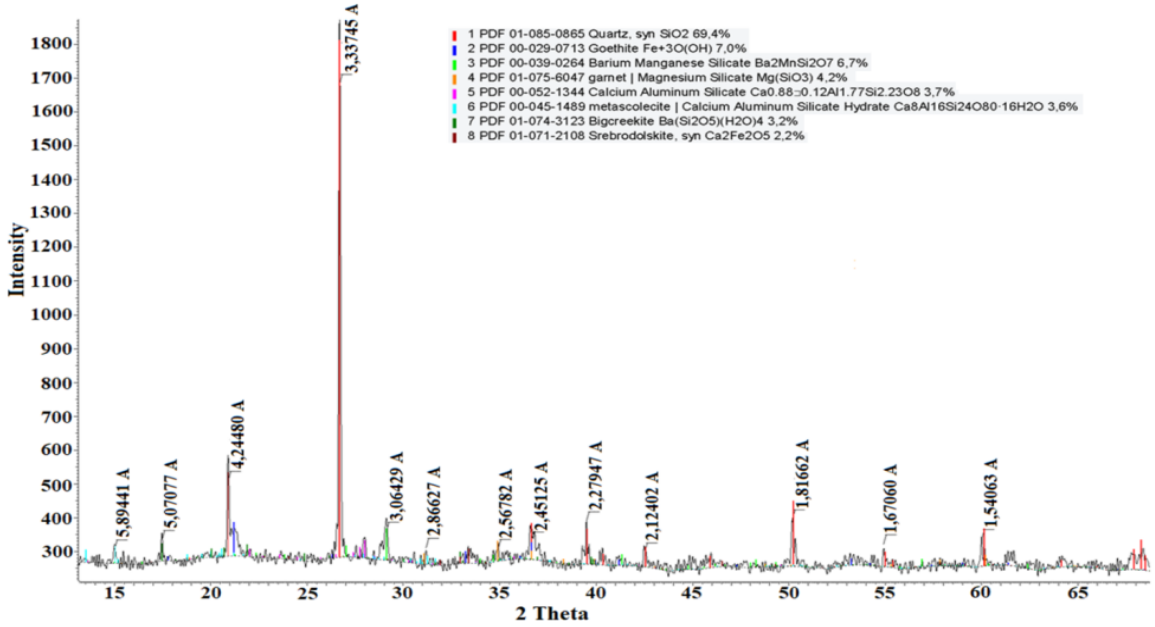

Figure 2. Diffractogram of a diatomite sample

To activate diatomite, we performed mechanical grinding and thermal activation of ferruginous varieties of diatomite in a laboratory furnace with subsequent grinding. The results of electron microscopy showed that during such thermal activation, diatomite particles acquire a spherical shape with a size of 5-10 nm (Figure 3). Thermal treatment of ferruginous forms of diatomite allowed to achieve a compressive strength of 25.2 MPa, and water absorption was 4.3 %.

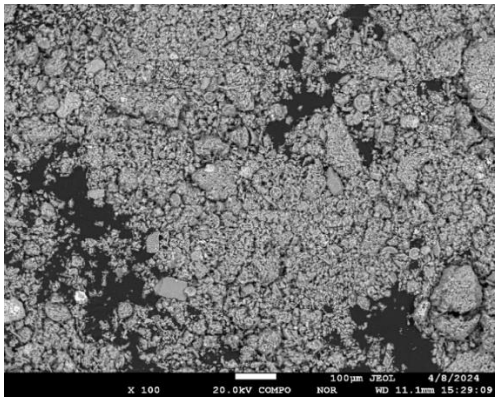

Figure 3. SEM image of a diatomite sample

Application of diatomite raw materials in the production of construction materials

The possibility of using activated diatomite in technologies for obtaining building products has been investigated. It is shown that the use of diatomite as a silicate component allows to achieve the grade of building products M 70, even without the use of autoclave conditions. The use of plasticiser and thermally activated diatomite in mixtures allows to significantly reduce water absorption of cubes. Semi-dry pressing followed by autoclave steam treatment of cubes sharply increases the compressive strength and grade of products and reduces their water absorption and specific gravity. There is a sharp increase in the strength of cubes when using thermally activated high-iron diatomite (20-30 % Fe O_{23}), which is associated with the partial formation of hydrated forms of ferrocalcites (Figure 4).

Figure 4. Samples of construction materials obtained using diatomite

Manufactured samples of cubes using thermally activated diatomite meet the indicators of GOST 379-95, required for silicate stones and bricks (GOST 379-95, 2004). The average density in the dry state is 1482 kg/m^3. The strength of adhesion with the base is 0.42 MPa. It is shown that compositions of dry building mixtures from cement, lime, ferruginous diatomite and gypsum demonstrate high plasticity when applying a layer of plaster, its rapid setting and strength when holding on a vertical surface.

The results have been obtained, indicating that the use of natural diatomite as a component for the production of expanded glass pellets from alkali-silica pellets significantly simplifies the technology of alumina production in the processing of ash from the combustion of Ekibastuz thermal coal. Marketable foam-steel pellets with a specific weight of less than 1 g/cm^3, which can be used as heat-insulating material in construction, were obtained. The studies carried out with the use of scanning electron microscopy testify to the uniform cellular structure of the obtained foamed glass.

Based on ferruginous varieties of diatomite, it is possible to obtain two-component iron oxide paint pigments of micro-dispersed spherical form, which can find application in construction.

To determine the possibility of obtaining highly dispersed particles of iron oxide pigments of spherical shape from ferruginous varieties of diatomites of the Zhalpak deposit, the material composition and thermal and mechanical treatment of samples of diatomite raw materials were studied to obtain a product suitable for use as a pigment, as well as the composition and properties of the obtained pigments.

X-ray phase analysis of samples of ferruginous diatomite obtained after their preliminary thermal and mechanical treatment was carried out. It is established that iron is in the form of jarosite in the initial sample, in the sample after hydrothermal treatment and calcination of jarosite. in the form of hematite. The phase composition of iron-containing components of pigment samples was determined.

Technological solutions for the utilisation of the mineral part of refined ferrochrome slag with obtaining construction products on its basis have been found. Application as reducing agents of aluminium powder in the amount of 2 g per 1 g of water-soluble chromium and 4 g $FeSO_4 \cdot 4H_2O$ per 1 g of water-soluble chromium allows to reduce the content of water-soluble chromium at soaking of cubes up to MAC values (Figure 5).

The dough mass when filling the cube moulds has high plasticity and allows taking a cast with the smallest fragments, which can be used in the manufacture of artistic products of complex shapes.

The technology of RFC slag utilisation allows to obtain not only metal concentrate, but based on the mineral part - various construction products: finishing sheets similar to SML (silico-magnesium sheets) and SCL (silico-calcium sheets), art castings, material for filling excavations in mines and quarries.

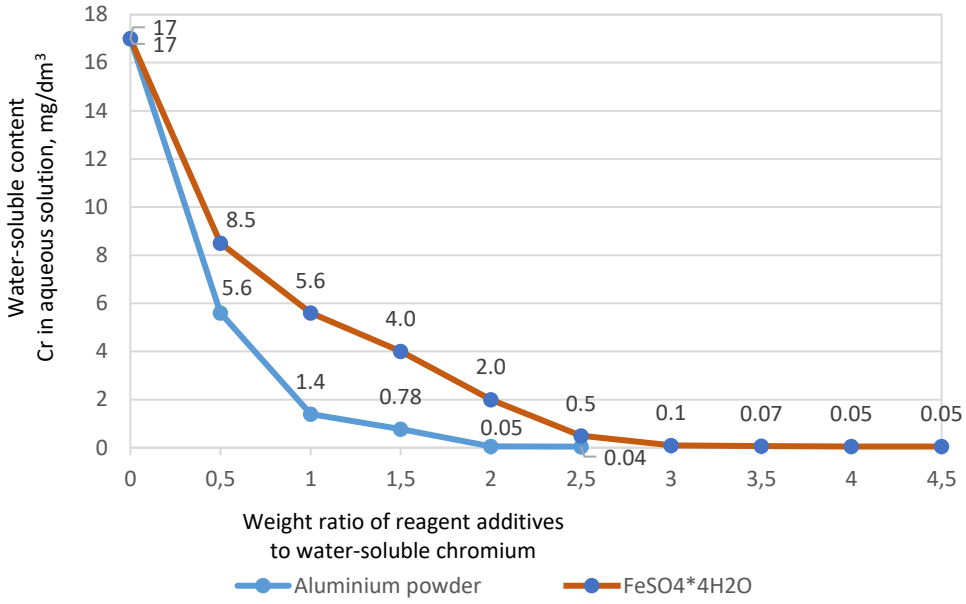

Figure 5. Effect of reagent additives on reduction of water-soluble chromium content

Tests on obtaining porous building rubble from the mineral part of RFC slags and natural diatomite were carried out, which showed that the most optimal conditions are the weight ratio in the mixture mineral part of slag/diatomite 2:1, which allows to synthesise strong light ferrosilicon-fluxing glass with good crushing strength, comparable to the strength of expanded clay. The optimum firing temperature is 1150 °C, which allows for obtaining light glass-like pellets with the lowest specific mass and the highest crushing strength.

The results of tests on obtaining magnesia building products (cubes, tiles) showed the possibility of utilisation of the mineral part of RFC slag (refined ferrochrome) after extraction of metal concentrate from RFC slag with obtaining building finishing tiles based on compounds similar to Sorel types of cement. The best characteristics of crushing strength (12.5 MPa) and water absorption (6.2 %) are obtained from the paste having in its composition: weight ratio of slag: $MgSO_4 \cdot H_2O$ - 4.38:1; addition of diatomite, % - 20.0; addition of liquid glass - 1.0; addition of carbomethylcellulose (M70) - 1.0.

Use of diatomites as a component of ferrosilicate-calcium binder in metallurgy

Based on chrome concentrate, mineral part of RFC, ferruginous diatomites and special coke at temperatures of 1050-1200 °C complex pellets with increased strength (up to 5325 N/pellet), not absorbing moisture and not losing mechanical strength when wet, which is associated with the formation of cementitious glass phase were obtained. It is not necessary to grind the components included in the pellet formulation to 0.07 mm, 0.25-0.1 mm is enough, as high strength is achieved by the formation of fluxing ferrosilicate-calcium glass phase.

The new technology of production of complex chrome pellets allows to effective utilize the mineral part of RFC slag with transformation of toxic hexavalent chromium into harmless glass mass; to carry out pre-reduction processes directly in the roasting process by obtaining partially metallized pellets; to solve the problems of dispersibility of initial materials; to utilize substandard pellet fragments (-0.3 cm) with production of additional conditioned products. The highest strength of pellets was achieved with ferruginous diatomite, which can be explained by the ultrafine dispersed form of iron oxide in diatomite and the high rate of formation of ferrosilico-calcium glass phase at relatively low firing temperatures.

The formation of ferrosilico-calcium glass phase, providing strength and lowering the melting temperature of chrome pellets during firing and melting in electric arc furnaces is caused by the formation of such compounds as magnesium hedenbergite and chloritoid-A.

Conclusion

Methods of obtaining various construction products based on diatomites have been developed: silicate bricks, dry building mixtures, iron oxide pigments, foam glass; binders for hardening chrome pellets; carriers of mineral fertilizers; reagents for treatment of wastewater from hydrogen sulphide. New data on

application of ferruginous variety of diatomites as the main component of dry building mixtures and highly dispersed particles of iron oxide pigments of spherical shape are received. The use of diatomites in the synthesis of silico-calcium-iron-magnesium compositions - effective binders in the production of hardened pellets based on finely dispersed chrome raw materials is proposed.

CRediT author statement: **S. Temirova**: Conceptualization, Methodology, Validation, Writing draft preparation; **D. Fischer**: Data curation, Visualization, Investigation; **Ye. Kuldeyev:** Supervision, Methodology, Reviewing, Software, Editing.

Cite this article as: Temirova, S., Fischer, D., Kuldeyev, Ye. (2024) The use of diatomites in industrial production technologies. *Challenges of Science*. Issue VII, pp. 46-51. https://doi.org/10.31643/2024.06

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