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Identification and Characterization of Sulfur Cake from Stepnogorsk Sulfuric Acid Plant

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Abstract

In the paper, the physical and chemical characteristics of sulfur cake from Stepnogorsk Sulfuric Acid Plant (SSAP LLP) were studied. During the production of sulfuric acid, 130–200 t of sulfur-containing residues are accumulated per year, the storage of which negatively affects the environment. The peaks of IR spectrum analyses are linked to the stretching vibrations of S=O, S-S bonds, and O-S-O groups. The chemical composition of the filtration waste of molten sulfur from the settling tanks of the Stepnogorsk sulfuric acid plant is represented by the following elements: S (about 60 wt.%), O, Na, Mg, Al, Si, Cl, Ca, Fe, Cu, Pb, and Zn. The content of organic compounds in sulfur cake is low, and mineral components – gypsum, calcium sulfate, and silicates are contained in insignificant quantities, which makes it possible to use it for the production of composite materials for construction. Using compositions will improve the properties of materials and provide an opportunity to sell additional volumes of sulfur on the domestic market, which will reduce the consequences of excess production and the environmental burden from long-term storage of sulfur-containing waste.

1. Introduction

In sulfuric acid production, the sulfur is pre-cleaned from ash and other impurities that deactivate the catalyst. Both sulfur and sulfuric acid are widely used in many industries. In the process of cleaning crude oil and gas from hydrogen sulfide, a by-product is obtained: elemental sulfur. The greatest danger in the Caspian zone is the production of the Tengiz field, which is very rich in sulfur-containing compounds. Besides Tengiz, there are other fields in Kazakhstan where the oil and gas are sulfur-rich. Tengiz sulfur, which has the highest purity in the world – 99.99%, is a completely competitive product. Sulfur is obtained in liquid, granulated, flaked, and crushed forms [1–10]. Most of the sulfuric acid produced in Kazakhstan is used for the uranium industry. The plant uses a modern and perspective technology for the production of sulfuric acid from lump sulfur. The transition of raw materials to the target product reaches 93%. The technology is safe for the environment from an ecological point of view. This approach allows for solving several problems of both environmental and economic nature [11].

As is known, solid elemental sulfur is harmless, but sulfur-containing wastes are problematic in environmental terms, which is characterized by its fairly high chemical activity. Molten sulfur vapor is passed through a filter material by the mixture of perlite, carbonate, and calcium hydroxide, which turns into sulfur cake with a sulfur content of 35–40 wt.%. Sulfur cake belongs to class IV, the sulfur in it is a class III hazard and is characterized by the ability to spon-

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taneously combust and is prohibited from burial in industrial waste. They can easily interact with many components of the environment to form some toxic substances. Along with this, especially in hot summer months, because of rising air temperatures, carcinogenic substances – mercaptans and highly toxic hydrogen sulfide – are also released from sulfur waste into the environment. These compounds are the main impurities in the considered sulfur-containing wastes in the sulfuric acid industry [9, 12–16].

Finding real ways to use sulfur waste allows us to improve the environment in the Caspian region not only in the places of their formation but also in the places of their storage. Using sulfur waste from the oil industry as a secondary raw material for the production of sulfuric acid and other commercial products is economically helpful compared with other technologies for their production from natural raw materials. Sulfur-containing industrial wastes of sulfuric acid plants should be utilized and fielded usable applications. Using sulfur-containing waste from oil, sulfuric acid, and other industries to get commercial products is of scientific and practical interest. For example, it is possible to synthesize new environmentally friendly sulfur-containing building materials of both organic and inorganic nature that can be sold to meet various industrial and economic needs [3, 17–23].

At the Stepnogorsk Sulfuric Acid Plant LLP (Stepnogorsk, Kazakhstan), there is a sulfuric acid production facility where production waste is formed – sulfur cake with a volume of about 130–200 t per year, the storage of which negatively affects the environment [10]. This work focused on studying the composition and properties of sulfur-containing waste from sulfuric acid production and their utilization to get new commercial construction products with improved characteristics and other useful properties.

2. Materials and methods

2.1 Research object

Sulfur cake is a waste product of the filtration of molten sulfur from the Stepnogorsk sulfuric acid plant. At the sulfuric acid plant, before using sulfur as a raw material for obtaining sulfuric acid, it is first purified from ash and other undesirable impurities. To carry out the process of purification from impurities, molten sulfur vapors are passed through a filter material. Then the filter cake is dried with steam. A mixture of perlite, carbonate, and calcium hydroxide is used as the initial filter material. After the technological cycle, the filter material turns into a sintered gray lumpy mass, and its composition, besides the main initial components, contains various sulfur compounds. The cake is a solid lump mass, non-volatile, and insoluble in water. It has Hazard Class IV.

2.2 Material characterization

The chemical composition of the original materials was determined by the Alpha II FTIR spectrometer. The FTIR spectrometer is designed to analyze materials in the infrared spectral ranges of 4500–450 cm^{-1}.

Images of the modified samples were taken with a JSM-6490 LA low-vacuum scanning electron microscope. The JSM-6490LA has a high resolution of 3.0 nm. The low vacuum mode allows you to observe samples that cannot be viewed in a high vacuum because of high moisture content or a non-conductive surface.

Elemental analysis of the samples was investigated using energy-dispersive spectroscopy (EDS) in scanning electron microscopy, which measures the energy distribution and intensity of X-ray signals generated by an electron beam incident on the surface of the sample.

X-ray fluorescence analysis of the samples was carried out on a Focus-M2 spectrometer by measuring the analytical lines of chemical elements and, by recalculating them, determining the mass concentration of elements contained in the analyzed sample.

X-ray phase analysis of the samples was performed on a D8 Advance (Bruker) apparatus, α-Cu, tube voltage 40 kV, current 40 mA. The obtained diffraction data were processed, and interplanar distances were calculated using the EVA software. Sample decoding and phase search were performed using the Search/match program using the PDF-2 Powder Diffractometric Database.

X-ray structural analysis of the samples was carried out on a PANalytical X'Pert Pro X-ray diffractometer. The default configuration of this instrument is Bragg-Brentano geometry with an X'Celerator high-speed, high-resolution detector using the Open Eulerian Cradle (OEC) sample stand. This combination typically provides excellent X-ray diffraction data quality in a relatively short acquisition time.

3. Results and discussion

Sulfur has a low melting point (112.8–119.3 °C) and melt viscosity ($6.5\cdot10^{-3}$ Pa·s). In solid crystalline form, it has a yellow color, sufficient mechanical strength, hydrophobicity, and water resistance. Sulfur cake is a waste product of molten sulfur filtration at the Stepnogorsk Sulfuric Acid Plant. Figure 1 shows photographs of elemental sulfur (a) and sulfur cake (b). A mixture of crystalline or granular sulfur particles makes up the sulfur cake. After filtering sulfur through perlite, the cooling and crystallization process causes these particles to vary in size and often have uneven, jagged edges.

The chemical composition of the sulfur cake was studied using the infrared (IR) spectroscopic method. IR spectroscopy has become one of the main physical research methods in chemistry, with the help of which the problems of qualitative and quantitative analysis of substances are solved and it is possible to judge the structure of molecules. Figure 2 shows the IR spectra of sulfur cake.

The IR spectrum of the sulfur cake displays numerous responses in the 2500–2000 cm^{-1} region, indicating silicon dioxide (SiO_2) bonds. The cake's IR spectrum revealed characteristic peaks of C-O-C bond deformation vibrations at 830–845 cm^{-1}. This could indicate that a copolymerization reaction is occurring along the saturated pearlite fragments, potentially forming a network or branched structure with polysulfide branches on the sides. The 1416.76 cm^{-1} peak is linked to bending vibrations of sulfur-containing compounds like sulfate (SO_4^{2-}) or sulfur-related bonds in the sample. It indicates sulfuric acid (H_2SO_4) or other sulfur-containing species like sulfates or thiosulfates. Usually, they might be represented by the absorption band around 1100 cm^{-1} in the IR spectrum. The highest peak 1087.06 cm^{-1} is related to stretching vibrations of S=O bonds. This peak presents the sulfur cake containing sulfate species, such as calcium sulfate ($CaSO_4$) or sodium sulfate (Na_2SO_4). Another possibility is the bending of oxygen-sulfur bonds in sulfur-contained compounds. The peak of 795.55 cm^{-1} can be attributed to the bending vibrations of O-S-O groups. Sulfate salts and compounds related to sulfuric acid contain these vibrations. This could suggest bound sulfate ions; they are common in the byproducts of sulfuric acid production. The peak around the frequency of 677.57 cm^{-1} can correspond to bending and rocking vibrations involving sulfur atoms from sulfur in different oxidation states or S-S bonds. Sometimes, they could be associated with the vibration of sulfur atoms in chains and clusters. The absorption bands in the sulfur cake's infrared spectrum, which absorption bands from 3200 to 3400 cm^{-1}, are associated with O-H stretching vibrations. These vibrations characterize hydroxyl groups (OH), which are found in water molecules and compounds containing hydroxyls. For instance, O-H stretching vibrations may be present in this region in hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$), a byproduct of the synthesis of sulfuric acid.

The scanning electron microscopy (SEM) method was used to study the surface structure of the sulfur cake. Figure 3 displays SEM images of the samples magnified 300, 500, 740, and 950 times. Figure 3 reveals a relatively rough and heterogeneous surface morphology of the sulfur cake, featuring a range of particle sizes and distributions. Because of the way the sulfur solidifies and cools throughout the filtration and cooling phases of the manufacturing of sulfuric acid, the sulfur cake had a layered or laminated structure with alternating thick and porous layers. Because the perlite particles are typically silicate-based, they may appear lighter in SEM images.

Fig. 1. Photographs of elemental sulfur (a) and sulfur cake (b).

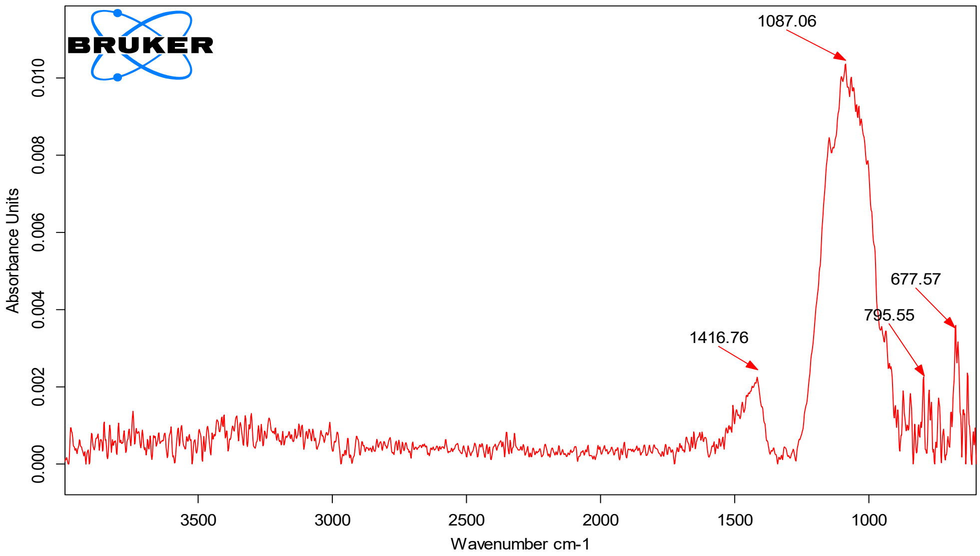

Fig. 2. IR spectrum of sulfur cake.

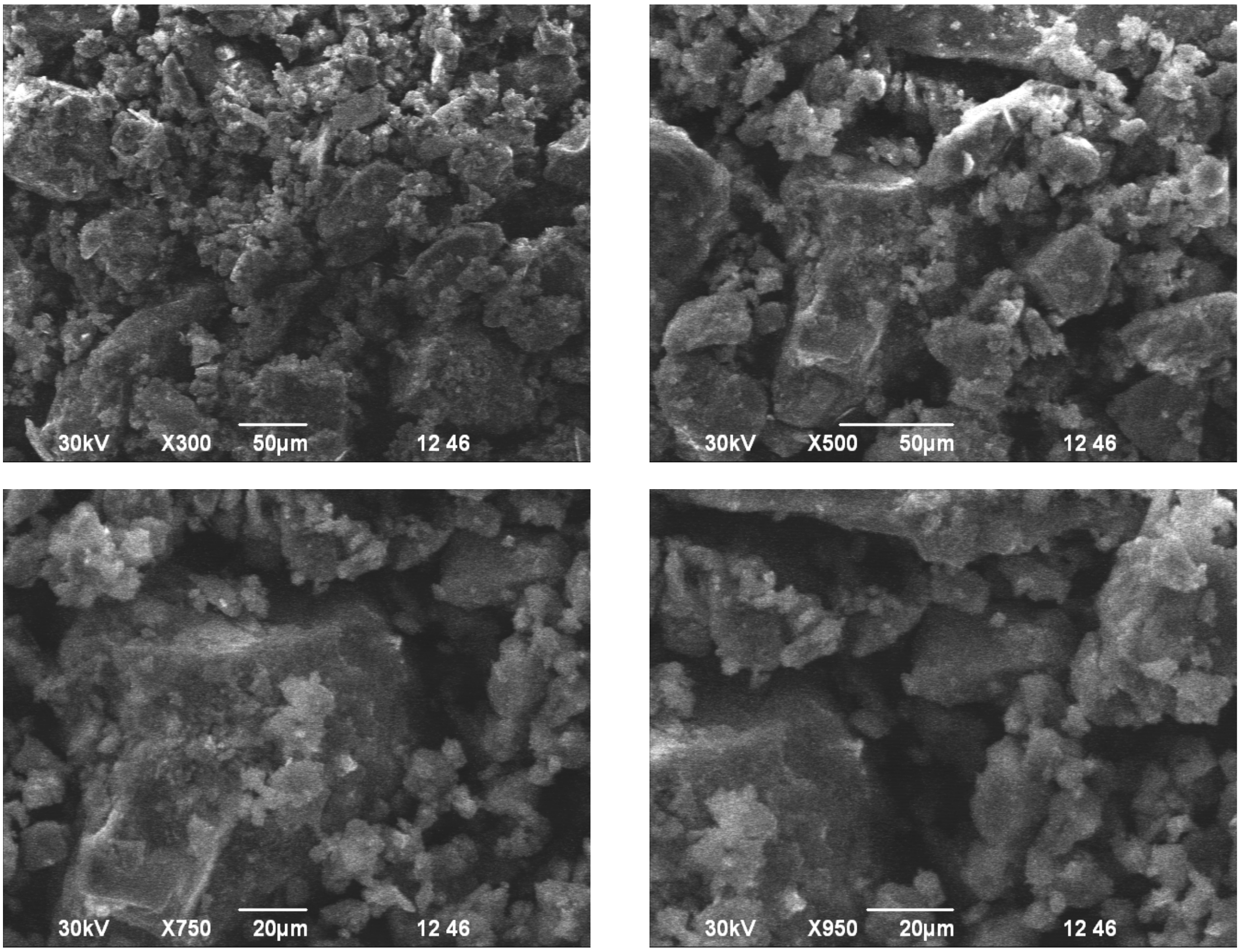

Fig. 3. Electron microscopic images of sulfur cake.

Perlite particles may stick together or form small groups inside the sulfur matrix, leading to certain differences in the sulfur's texture cake. The sulfur cake may contain a portion of the fine, irregular perlite particles used for filtration. Some of the sulfur cake may have smaller pores on the outside and on top of the sulfur particles. This is because the perlite filters through it and the sulfur crystallizes. Less compacted sulfur may cause larger macropores in the sulfur cake, which would give the surface a rougher feel.

Scanning electron microscopy might also be coupled with energy-dispersive X-ray spectroscopy for elemental analysis (EDX), which would show a high proportion of sulfur, oxygen, and other elements on the sample surface. The EDX also determined the elemental composition of the sulfur cake. However, the results showed that the sulfur content of the sample reached 95% and the oxygen content was 2%. Besides sulfur, the cake contains copper, zinc, and a small amount of lead. These metallic elements appear in natural rocks that form perlite, which is the basis of sulfur cake. Since they are an oxide compound, oxygen is present in the cake.

A scanning electron microscope accompanies this method, allowing for an examination of the sample's surface layer. The amount of sulfur in the cake appeared higher than its actual content. Therefore, it is necessary to continue studying the composition of the cake using X-ray analysis.

The X-ray fluorescence method also determined the elemental composition of the sulfur cake. Table 1 shows the elemental composition of sulfur cake. According to the tabular data, the amount of sulfur in the cake is 57.849%. The second largest amount is oxygen in oxide compounds (21.799%). It has been established that the cake contains Na, Mg, Al, Si, Cl, Ca, Fe, Zn, and Cu in small quantities. Among them, the maximum amount is Si (2.134%), then Ca (1.147%). The copper content is only 0.008%.

The composition of the sulfur cake was studied by X-ray phase analysis and it is shown in Fig. 4. The results of the X-ray phase analysis of the sulfur cake showed that it consists of 84.0% sulfur, 7.0% calcium sulfate ($CaSO_4$) and 4.8% gypsum ($CaSO_4 \cdot 2H_2O$). Iron (II) disilicate ($Fe_2Si_2O_6$) in the amount of 4.2% was also found in its composition. 1.147% of Ca in the

Table 1. Elemental composition of sulfur cake

#	Elements	Concentration, %
1	O	21.799
2	Na	0.217
3	Mg	0.060
4	Al	0.532
5	Si	2.134
6	S	57.849
7	Cl	0.043
8	K	0.101
9	Ca	1.147
10	Fe	0.628
11	Cu	0.008
12	Zn	0.018

sulfur cake determined by X-ray fluorescent analyses is sufficient to form 3.9% of sulfate, which aligns with the results of X-ray phase analysis. However, the observed 2.4% of the disilicate (determined by X-ray phase analysis) from 0.628% of Fe is slightly higher than the expected stoichiometric quantities. A larger disilicate content in the X-ray phase analysis could result from the existence of extra silicate sources, most likely from the perlite filtration medium, or the potential production of hydrated or mixed phases in the sulfur cake. Because of X-ray phase analysis detects the crystalline phases in the objects, and X-ray fluorescence detects and quantifies the elemental composition. Therefore, it can be concluded that the higher quantity in the phase analysis reflected the complex nature of the sulfur cake samples. It might contain hydrated materials and additional phases that are not predicted by the elemental composition.

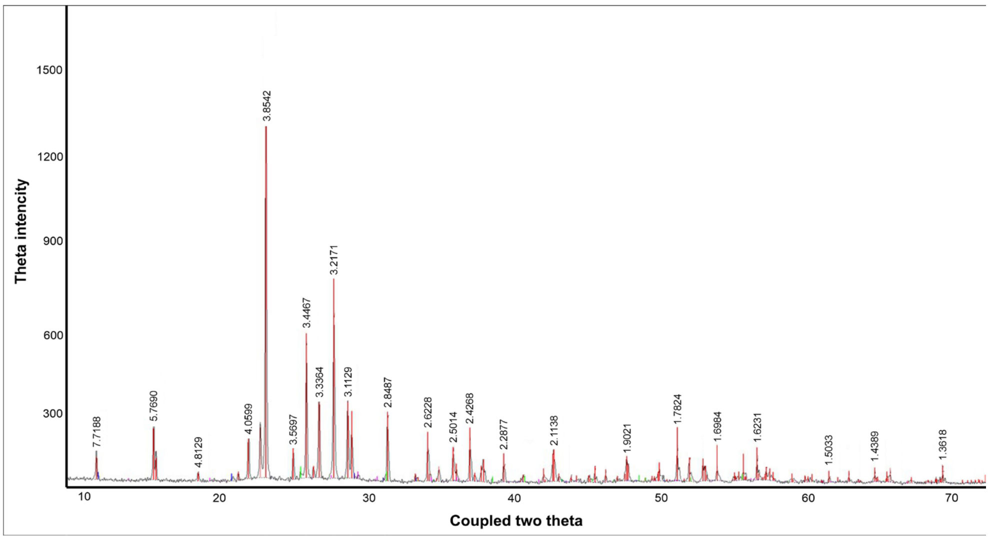

Fig. 4. X-ray phase analysis of the sulfur cake.

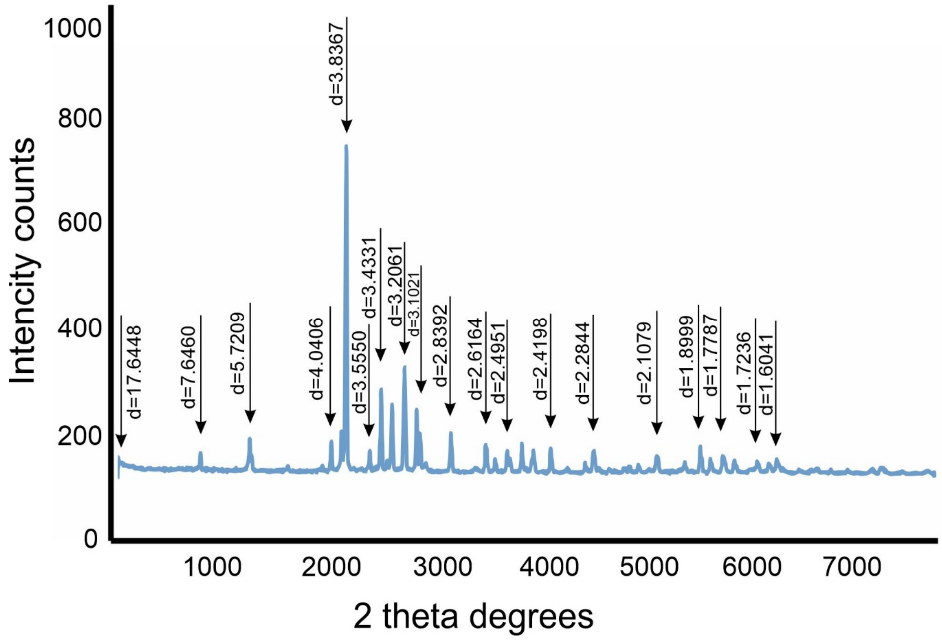

Fig. 5. X-ray Diffraction patterns of the sulfur cake.

The X-ray diffraction (XRD) analysis was provided for sulfur cake (Fig. 5), that XRD indicates a range of diffraction peaks at specific 2θ angles corresponding to various crystal structures or phases present in the sample. XRD peaks represented various phases related to sulfur, sulfur oxides, sulfur compounds such as sulfide and sulfates, perlite or its altered form, sulfuric acid byproducts, and other compounds involved in the filtration process. Although precise values depend on the particular sulfur allotrope elemental sulfur frequently displays distinctive diffraction peaks, usually around 2θ values about 23.5°. They correspond to the monoclinic α-sulfur phase, as a component of the sulfur cake. Sulfuric acid byproducts exhibit peaks in the lower-angle region, typically below 20° 2θ. Here is an interpretation of some of the listed diffraction peaks at 2.84, 3.21, 5.72 Å (2θ ~ 15°, 29°, 31°) could be linked to sulfur compounds or hydrated sulfates. 3.83 and 4.04 Å (2θ ~ 22°, 24°) may correspond to crystalline sulfur or other sulfur oxide phases. Diffraction peaks at 1.60, 1.78, 2.28, 2.42, 3.10 Å (2θ ~ 30°, 36°, 39°, 51°, 55°) are likely sulfur, sulfate or sulfides.

Despite not having a distinct crystalline structure in XRD, perlite is an amorphous volcanic glass that may develop specific crystalline phases associated with the material following processing. Perlite can contribute to peaks observed at lower angles around 3.5–5 Å. The diffraction peaks at 2.62 and 17.64 Å (2θ ~ 5°, 34°) can be thought of as the reflection of a larger crystalline structure or a certain mineral phase, like some sulfates or silicates. 2.11, 2.50, 3.32, 7.64 Å (2θ ~ 11.5°, 28°, 35°, 41°) and others may also correspond to silicates or possibly a sulfate mineral. The peak at 5.72 Å corresponds to perlite or other crystalline impurities.

4. Conclusions

The study examined the compositions and physicochemical characteristics of sulfur-containing waste, which was obtained from the filtration of molten sulfur from the settling tanks of the Stepnogorsk sulfuric acid plant (LLP "SAP") – sulfur cake.

A combination of sulfur crystals, porous structures, possible perlite residues, and different levels of surface roughness, all influenced by the filtration and chilling processes, would be seen in a SEM investigation of the surface structure of sulfur cake from sulfuric acid production that has passed through perlite. The chemical composition of sulfur cake is represented by the following elements: S, O, Na, Mg, Al, Si, Cl, Ca, Fe, Cu, Pb and Zn. IR-spectroscopic analysis concluded that the sulfur cake is likely composed of sulfuric acid byproducts, including sulfate salts and sulfur-containing compounds. There may be minor surface fractures or gaps in some areas of the sulfur cake due to erosion or fissures brought on by the filtration process, residual sulfuric acid, or other contaminants. The filtration process, the interaction between the sulfur and perlite particles, and the cooling sulfur could all contribute to the roughness. Because sulfur cake has a low organic compound content and trace amounts of the mineral components such as gypsum, calcium sulfate, silicates and metal oxides, it can be used to create composite materials for building. Given the composition of sulfur cake, developing a technology to use it as a building material not only solves environmental issues but also yields economic benefits. Sulfur cake's ability to replace some mineral materials and cement as a binder explains this economic benefit.

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