

Possible Alternatives for Cost-Effective Neutralisation of Fluoroanhydrite Minimising Environmental Impact

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This article discusses the options for neutralising the waste fluoroanhydrite also containing residues of sulphuric acid. A process is proposed by which all reagents provide a neutral or alkaline environment with pH ≥ 7 which remains unchanged for more than 28 d. This indicates that complete and irreversible neutralisation of the toxic fluorine-containing waste materials was ensured. The used reagents were CaO, CaCO₃, KOH, Na₂CO₃ and Ca(OH)₂. The most efficient reagents, also resulting in stability of the product are CaO and Ca(OH)₂. The obtained results lead to proposing the use of the process output as a component for the production of ceramic products for the construction industry. This will allow obtaining additional benefits from replacing primary natural materials and the associated emissions for their sourcing and production.

1. Introduction

The accumulation of industrial waste is a serious environmental pollution problem. Often, the accumulated amounts of waste are approaching the current tailing pond capacities. One is to expand them which threatens ecosystems and increases costs. These waste materials often contain high-value components that can be recycled to reduce pollution. Their neutralisation and reuse will provide a synergy following the Circular Economy ideas – simultaneously reducing toxic pollution and the need for fresh raw materials.

In China, in the production of vanadium, the residual vanadium content in the waste has caused many environmental problems. That caused by the impossibility of further use of slag for the extraction of the remaining valuable metals and the disposal of steel slag containing residues of heavy metals that cannot be further extracted by leaching. Finding a promising way to use these secondary resources is an important task. Yang et al. (2013) proposed a method for the production of black ceramics using vanadium-containing waste. The method significantly reduces the cost of producing black ceramics and at the same time solves some environmental problems. The final product was labelled as V-Ti black ceramics and has many applications, such as black pigments, black tiles, infrared emitting elements and solar absorbers and others.

Another potential contribution to sustainable development is in the production of building materials, in particular, the cement industry. Koci et al. (2016) explored the possibilities of using ceramic dust waste as a substitute for cement in lime-cement plasters. For this purpose, 4 samples were prepared with different compositions and were experimentally analysed to determine their basic physical, mechanical, hydro and thermal properties. The data were used to evaluate the hydrothermal and other characteristics of the stucco mixtures. The calculations were carried out using numerical simulation in a combination of heat and moisture in the dynamic climatic conditions of Prague. The experiment results showed that waste ceramic dust as a substitute for cement does not adversely affect the properties of plasters. Replacing cement has led to energy savings associated with its production, which can reach up to 3,115 MJ of thermal energy in the case of a hypothetical house.

Krivenko et al. (2017) attempted to form cement-stone structures from alkaline aluminosilicate - an analogue of natural zeolites by adding calcium silicate hydrates. The obtained Portland cement was reported as an excellent building material, and concrete based on this component having good mechanical properties and durability.

However, when Portland cement is subjected to extreme operating conditions (high/low temperature, aggressive media, radiation, etc.), its disadvantages become apparent. They studied the mechanism of destruction of silicates and aluminosilicates, determined the rates of structure formation processes and other synthesis conditions. The disadvantages were found to be caused by meta-stability of Portland cement hydration as a result of the conversion of calcium hydrate, relatively high solubility of hydration products and low corrosion resistance in the presence of $\text{Ca}(\text{OH})_2$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$. It is known that the production of Portland cement is accompanied by high energy consumption (7,500 J/t), emissions with a high embedded (virtual) content of CO_2 : 0.5 t CO_2 / t cement. Its production leads to depletion of natural resources. This makes necessary the search for new types of raw materials, reducing energy, environmental and economic costs.

To maximise the business benefits, waste management may include co-production of building materials. The environmental impact of metallurgical waste was investigated by Zhang (2019). His work presents the main types, sources and characteristics of metallurgical solid waste. Basically, methods for the disposal of blast furnace slag, converter slag and slag from an electric furnace by introducing building materials and the ceramic industry into production are proposed. Granular blast furnace and steel slag, as a rule, is used as raw material for the production of cement and glass-ceramics. It is noted that the traditional process of cooling slag with water leads to heat loss of slag, environmental pollution and inefficient consumption of water resources. In this regard, it is urgent to develop a technology for the utilization of waste heat from blast furnace and steel slag.

There have been recent studies showing potentially promising results in the joint utilisation of waste from various industries, obtaining completely new products. Zeng et al. (2019) studied the possibility to recycle medical waste and metallurgical ash. The authors found that secondary fly ash after plasma gasification contains high concentrations of heavy metals and can serve as a potential resource for metallurgy. In addition, the combined treatment of hazardous waste with plasma gasification allowed them to develop a "zero discharge" technology for the treatment and processing of various hazardous waste products to produce an effective catalyst.

Another important development is the search for opportunities to recycle waste in the same area where it is generated to minimise economic costs and reduce environmental damage to the environment. Šomplák et al. (2018) evaluated the greenhouse gas emissions caused by fuel consumption during waste transportation and proposed a mathematical model for planning the waste treatment facilities and transportation routes.

In Kazakhstan, where the metallurgical industry is the leading one, there are problems associated with both the efficient processing of raw materials and the disposal of generated waste. This makes it necessary to search for ways to use the waste as a raw material elsewhere. In metallurgy, hydrofluoric acid (HF) is produced and used to extract a number of rare metals from concentrates. The waste from that production contains fluorine-containing components. These materials are toxic and hazardous.

Traditionally, hydrofluoric acid is prepared by reacting fluorspar (CaF_2) with concentrated sulphuric acid to form fluoroanhydrite. After the reaction, HF is discharged and condensed, while hydrofluoride is usually diluted with water, neutralized with lime and pumped to ponds for disposal. Usually, when obtaining 1 t of 100 % HF, almost 4 t of CaSO_4 is formed, which is stored in dumps without any application (Zabolotnaya et al., 2014).

Many fluorite concentrate hydrofluoric acid plants have been designed without the disposal of calcium sulphate waste. The predominant technology utilises wet neutralisation and disposal of a suspension of fluoroanhydrite in the tailings. Typically, crude anhydrite is neutralized with CaO , $\text{Ca}(\text{OH})_2$ or CaCO_3 , and then finely ground. Valorisation of fluoroanhydrite was also carried out. Raisa et al. (2012) described the characteristics of hydrofluorite, a by-product of a Tunisian hydrofluoric acid preparation plant, and formulated bulk compositions for pouring and producing a bulk floor. The experimental results confirmed that the compositions based on fluoroanhydrite have acceptable mechanical and rheological properties and can be used for the coarse screed. Saulin et al. (2016) note that suspensions of $\text{Ca}(\text{OH})_2$, CaCO_3 or a mixture thereof are used to remove fluoride ion from acidic industrial solutions. In this process, $\text{Ca}(\text{OH})_2$ and CaCO_3 will interact with the acids in the solution, neutralising them, and the calcium ion will react with the fluoride ion to form a CaF_2 precipitate. However, in the neutral medium obtained after the neutralisation of acids, the solubility of these compounds is low. Therefore, the removal efficiency of fluoride ion will be low. Thus, to obtain a pure product with a high CaF_2 content in this process will be very problematic, which will complicate its further use, since the product will contain not only the CaF_2 formed but also a significant amount of the starting reagents. It should be noted that insoluble fluorides also have a second hazard class, so the disposal of sludge containing CaF_2 is also very problematic. In another work, Saulin (2015) considered the features of each stage of the process of utilization of fluoride ion from solutions, justified the selection of calcium-containing reagents, and determined the sequence and conditions of their use. The kinetics of the interaction of calcium carbonate with acidic and neutral solutions containing fluoride ion was studied. The conditions are presented when calcium carbonate can fulfil two functions: to be a calcium-containing reagent and to be a collector, the particles of which serve to precipitate finely dispersed CaF_2 enabling the separation of suspensions. The of the process allows achieving 100 % extraction of fluoride ions from the solutions. The proposed technology for the disposal of fluoride ions from industrial acidic industrial

waste can be realised with the help simple hardware at low cost. The effectiveness of using CaCO_3 obtained by precipitation from solutions and powdered reactive calcium carbonate is compared. The author selected the most complex version of the acid solution with a high concentration of fluorides, the neutralisation of which is difficult due to the high concentration of fluoride ions and the high acidity of the solution.

While various versions of the technology for neutralising fluoride anhydrite have been known for decades and have also been gradually improved, developments stop at the production of binder material and do not reach the development of a complete technological scheme, which ends with useful final products. This study aims to adjust the process of neutralisation so that the subsequent stages of the production of ceramic products can directly use the obtained intermediate material.

Existing technologies (Fedorchuk et al., 2017) to neutralize fluoroanhydrite are constantly being improved, but they are not universal. Depending on the type of raw material, the profile of the enterprise in which they are formed, the annual accumulation of volumes and other factors, the final products of neutralization may be various substances (Albustami et al., 2014).

This study proposes a new approach to the process of neutralising fluorine-containing materials that enables their use as additional components in the production of ceramic products with wide applicability in the construction industry and beyond. This study uses fluorine-containing waste from the production of HF acid at a Kazakh metallurgical plant for the production of Rare Metals.

In the current technology, this waste is neutralised with a calcium-containing reagent, mainly CaCO_3 , followed by transportation to a landfill at a distance of about 350 km. Within the process of neutralisation, a certain amount of waste turns into commercial-quality gypsum, which is sold to the consumer. Depending on the composition and quality of feldspar, from which hydrofluoric acid is obtained, it is not always possible to ensure high-quality neutralisation of the toxic waste. Due to the characteristics of the process used by the plant, which cannot adequately respond to the variations in the feldspar raw material, there is a danger of incomplete neutralisation of the sulphuric acid and high probability of a reverse transformation of the metastable toxic waste with a return of the acidity. This danger limits and sometimes hinders the reuse of that waste in other industries. Aiming to resolve this problem, the current work presents improving the neutralisation process, evaluating the effect of several key reagents and the neutralisation conditions – such as particle size, amounts of neutraliser used and reaction time, on the properties of the treated material and recommends the most suitable combination.

2. Materials and methods used

As a starting material, hydrofluoric acid hydrofluoride was selected containing a high concentration of fluorine-containing components, as well as an excess of sulphuric acid, indicated by the detected pH 0.3 - 2.0. In this regard, experiments were conducted on the neutralization of fluoroanhydrite.

The starting fluoroanhydrite is weighed on technical scales to an amount of 50 g. Then it is poured into a porcelain cup and triturated with a porcelain pestle. A sample with a quantity of 5 g measuring cup is taken from the grated fluoroanhydrite. Then, 15 mL distilled water is added and mixed thoroughly. After the mixture is settled, the acidity is determined using indicator paper or a pH meter.

Next, it is necessary to neutralise the fluorohydrite. An amount of 5 g of milled fluoroanhydrite is placed in a glass beaker, 15 mL of distilled water is added, and a certain portion of the neutralising reagents is added while stirring. After each addition of the neutralizer and the lag of the mixture, the pH is determined. The neutralisation process is carried out until $\text{pH} \approx 11$, for assuring sufficient reserve compensating the follow-up acidic reversal. By summing the mass (in g) of the neutraliser to a certain pH, its consumption was determined.

The nature of the neutralising reagent, the duration of the process, the method of neutralisation, the particle size distribution of the feedstock are the main factors in the process. The following reagents were used: CaO - purity 98.1 % (GOST 8677-76 amendment 1); chalk (CaCO_3), quicklime, 0.1 M KOH solution. The latter was prepared according to GOST 24363-80. For the preparation of 250 mL of KOH 0.1 M solution, 1.4 g of KOH and 248.6 mL of distilled water are required. Other reagents included dried soda; lime milk (7 % – prepared from pure CaO. To prepare a 200 mL lime milk, 11.213 g of pure CaO were used, mixed with 196.787 mL distilled water.

The results were evaluated using 3D plots for identifying the key factors, relationships and trends in the experimental data. Using Scanning Electron Microscopy, the morphology of the sample particles was investigated. A JSM-6390LV microscope with the INCA Energy energy-dispersive microanalysis system with an accelerating voltage of 5 to 20 kV, equipped with detectors of back-scattered and secondary electrons and on a Superprobe 733 electron probe microanalyser of the JEOL company (Japan) was used. Analysis of the elemental composition of the samples and photography of various types of radiation were performed, using an energy dispersive spectrometer INCA ENERGY from Oxford Instruments (England) mounted on a Superprobe 733 electron probe microanalyser at an accelerating voltage of 25 kV and a probe current of 25 nA.

3. Experimental data

At the first stage, the following neutralising reagents were evaluated: CaO, CaCO₃, quicklime, 0.1 M potassium hydroxide (KOH); dried soda Na₂CO₃, slaked lime Ca(OH)₂. After weighing the sample metallurgical waste and the neutralising agents, the process was carried out in the presence of distilled water for each case, also determining the degree of change in the pH. According to experimental data, the dependence of pH on the nature of the neutralizing reagent in the form of a hexagram was constructed (Figure 1).

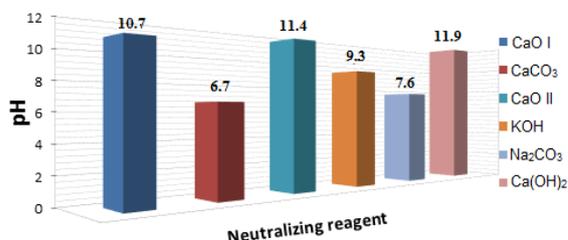


Figure 1: pH dependence on the nature of the neutralizing reagent

Figure 1 shows that Ca(OH)₂ interacts with fluoranhydrite with the highest efficiency. If this is used, a highly alkaline environment is achieved (pH = 11.9). The use of quicklime as a neutralizing agent also provided a high degree of neutralization (pH = 11.4). A slightly lower pH = 10.7 was observed when using pure CaO. Other neutralisers showed lower effectiveness. When using Na₂CO₃ and CaCO₃ as reagents, the pH of the medium did not exceed 7.6 and 6.7. The use of KOH as a neutraliser showed an average result, and the pH was 9.3. Another important factor in the neutralisation process is the granularity of the source of technogenic material. To conduct a sieve analysis, 500 g of a homogeneous initial fluoranhydrite were selected. Then using a set of sieves fineness: 0.063; 0.1; 0.16; 0.2; 0.315; 0.63; one; 1.6; 2.5 mm sieved all the specified amount for 5 minutes. After sieving, the mass of the coarse fraction was weighed on an analytical balance, and the small class was sieved to a class of -0.063 mm. The result of the sieve analysis is shown in Figure 2.

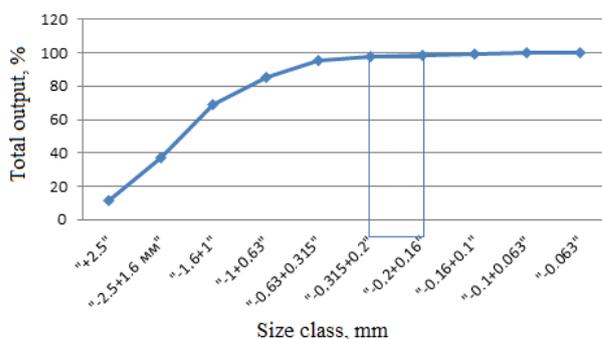


Figure 2: Granulometric composition of acid fluoroanhydrite of the Kazakhstan plant

The granulometric composition of the sample waste material affects the interaction of the neutralising reagent with fluoroanhydrite and the effectiveness of the neutralisation. The identified composition shows the need for further grinding, to increase the speed and extent of the reaction. It is important to consider the simultaneous effects of several factors. In this study, (StatSoft, 2018) the effect of the calcium compounds concentration (Figure 3) and the duration of neutralisation tests (Figure 4) on the pH of the medium were evaluated. The neutral reaction was achieved by selecting factor values, to ensure that no reversal to acidic reaction would take place due to physical factors such as poor mass transfer rate, for up to 28 d.

As can be seen from Figures 3 and 4, a change in the colour of the plane from green to red means the transition of the pH of the medium from acidic to alkaline. Figure 3 shows that the greatest neutralisation efficiency is achieved with CaO I. Figure 4 shows the effect of the neutralisation duration on the pH of the medium. At the next stage, the medium pH was measured after several days of exposure to the reagents. In the neutralised mixture, the following regularities are observed: a decrease in pH and a change from neutral to acidic is observed for samples neutralised using CaO I, KOH, Ca(OH)₂; pH increase to an alkaline medium for CaCO₃, and CaO II neutralisers; for the case of Na₂CO₃, the pH practically does not change.

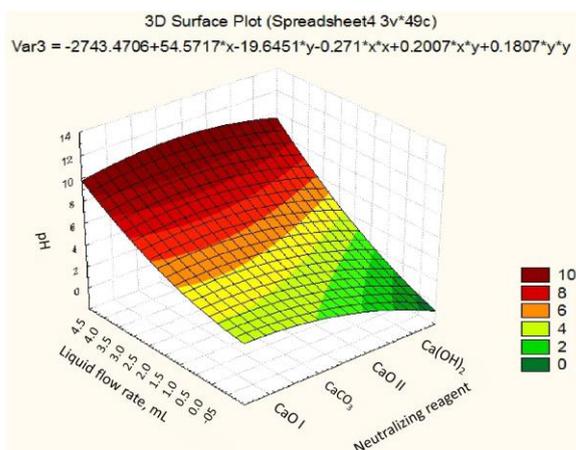


Figure 3: The effect of the concentration of calcium compounds on the pH of the medium

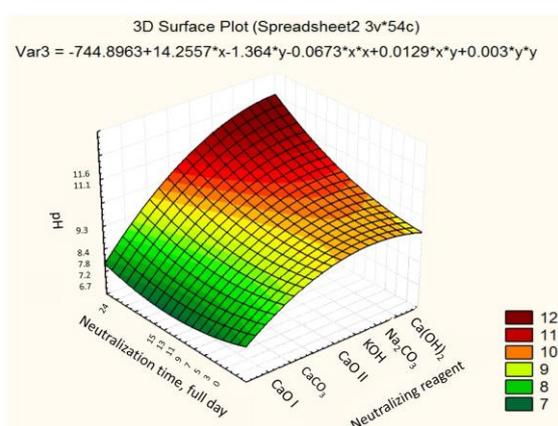


Figure 4: The dependence of the duration of neutralization on pH

It should be noted that neutralisation with calcium-containing reagents was accompanied by precipitation in the form of flocculent particles. Analysis of the structure and composition of sediment samples was carried out using a scanning electron microscope. A micrograph of the obtained precipitate is shown in Figure 5. As can be seen in the micrograph, the sediment contains aggregates of needle-shaped particles of various thickness. The large aggregates reach more than 30 μm . Many smaller pieces are visible. The analysis of the precipitate showed that the solid phase is mainly represented by gypsum. Thus, the studied neutralising reagents efficiently convert the residues of sulphuric acid to gypsum and ensure the achievement of a neutral or alkaline environment ($\text{pH} \geq 7$). This practically remains unchanged throughout the experiment up to 28 d and longer. Complete and irreversible neutralisation of toxic fluorine-containing waste with the greatest effect and stability is achieved by calcium compounds – CaO and Ca (OH)₂. It is shown that the neutralisation products consist mainly of commercial-grade gypsum, which can be sold to the consumers. There is also a fraction of completely neutralised inert waste, which is suitable for reuse as a component of dry plaster mixes and other purposes. At the next stage of the study, it is planned to use neutralized waste as an additional component in the synthesis of new ceramic materials suitable for use as catalyst carriers for environmental catalysis and Lego-bricks for the construction industry.

4. Conclusions

It was established that all the studied neutralising reagents effectively convert the residues of sulphuric acid and ensure the achievement of a neutral or alkaline environment with $\text{pH} \geq 7$, which practically remains unchanged throughout the experiment up to 28 d and longer. This is especially important for the possibility of subsequent synthesis of new ceramic materials based on neutralised industrial waste.

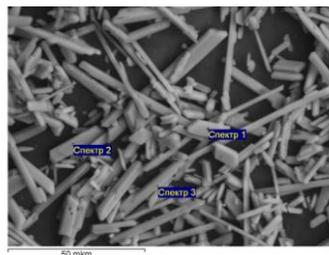


Figure 5: Micrograph of sediment particles obtained in the process of neutralization using CaCO_3

The results obtained during experiments showed promising process parameters and prospects for further recycling and reuse of the waste instead of storing it in landfills. At the next stage, it is planned to involve completely neutralised waste in the synthesis of new materials in the composition of ceramic materials suitable for use as catalyst carriers for environmental catalysis and “Lego” bricks for the construction industry.

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