

Development of the method for obtaining and studying vitriol of the iron sulphate based on iron-containing wastes

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Abstract. Especially in recent years, a ferric sulfate solution has occupied the attention as a useful water treatment agent and, particularly, a ferric sulfate solution and a basic ferric sulfate solution have a quick sedimentation speed for the resulting flocs and show good deodorizing ability as compared with a water treatment agent of an aluminum type such as an aluminum sulfate solution and a basic aluminum chloride solution whereby they have been widely used as a water treatment agent for waste water from paper manufacturing industry, from food industry, from chemical industry, leather industry. The purpose and task of the research is to develop the technology for the production of iron sulfate salts. For this purpose used iron filings and sulfuric and hydrochloric acid were used for this purpose. Processes of dissolution of ferric waste in acid are well studied and are shown.

1 Introduction

Currently, there is almost no system of objective criteria for the prospects of various technological and constructive developments, the selection of the most advanced of them, etc. on the contrary, and it is an ineffective and environmentally unacceptable prohibition [1]. The latest recommendations of international organizations on the general principles of evaluation and certification of products and technologies are little known in the world, which negatively affects the competitiveness of products; there is a lack of information on these very pressing issues [2-3]. However, environmental requirements, primarily the reduction, rather than the expansion, of developed areas limit the possibilities of developing new deposits. Thus, the shortage of natural resources in the world is becoming a serious state-level problem.

At the same time, in the world, where a large amount of metal is accumulated in man-made waste, about hundred billion tons metallic wastes are generated annually. Man-made waste processing is the only long-term solution to the problem of raw material sources. The basis of the direction called "recycling" in developed countries is waste processing [4-5]. The production of high-quality products has become the demand of the era when the signs of scarcity of natural resources, which pose a threat to the environment, have appeared.

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Thus, the product is the same resource as the consumption of energy and materials, and environmentally friendly production, as mentioned above, includes the production of high-quality products confirmed by product certification [6].

Techno-genic raw materials, accumulated at many enterprises in quantities reaching tens and hundreds of millions of tons of metals, are usually characterized by a low content of useful components [7]. It is noteworthy that almost 90% of the cost of production of rare metals is the cost of the feedstock; therefore, increasing their extraction rates is the most important area of processing technology. It is obvious that such complex scientific and technical problems need to be solved by creating fundamentally new technological directions related to the production of artificial raw materials suitable for obtaining standard final products [8]. The above iron-containing resources include metal industrial waste, as well as iron ores available in Uzbekistan. Thus, the involvement of industrial waste in the production of to some extent contributes to environmental improvement, on the other hand development of acceptable technology for processing iron-containing industrial waste in order to obtain import-substituting products is an urgent task. Based on this, research has attempted to develop a method for the synthesis of iron sulfate (2) and the production of vitriol based on it

2 Experimental part

2.1 Raw Materials and Reagents

The object of the study was household metal waste containing iron containing more than 80% iron. The materials used in this study were iron waste from scrap metal and dilute sulfuric acid (30% H_2SO_4). Depending on the origin of these wastes, they are very diverse in terms of their properties, size, particle shape and composition of components such as cast iron, alloy steel, non-ferrous metals, non-metallic inclusions and residues. There are three sources of metal waste: circulation, metal recycling industry and depreciation. One of the serious problems associated with the use of this waste is its purification from metallic and non-metallic impurities. Metal waste contains a significant amount of moisture and lubricants (automatic AK-15, AK-10, industrial oils 24, 30, etc.). Various thermal methods are widely used to remove oils from these wastes.

2.2 Preparation Process

Under laboratory conditions, iron (II) sulfate is obtained by dissolving iron fragments in 30% sulfuric acid. Iron pieces are cleaned of rust and dissolved in the 30% sulfuric acid solution. In this case, iron scraps should be superfluous. The mixture is heated at a temperature not higher than 50-60°C until the interaction of iron with acid stops. The solution is then quickly filtered, treated with dilute sulfuric acid, and saturated with hydrogen sulfide to precipitate excess metal sulfides [9]. The precipitate of sulfides is filtered and evaporated to half the volume. After cooling, the ferrous sulfate crystal was quickly separated, washed with ice water, then alcohol, and dried at 30°C.

2.3 Methods of investigation of process

The leaching of iron from iron-containing industrial metal waste was studied depending on the sulfuric acid concentration, S: L ratio (solid and liquid), leaching time and temperature. Analytical methods: iron was determined by spectrophotometric [10] and trilonometric [11] methods using sulphosalicylic acid. The chemical composition of the solid precipitates was

determined by full acid digestion of the sample and analyzed for components corresponding to solutions. The density of the obtained iron sulfate solutions with different concentrations was determined by the pycnometric method. X-ray phase analysis was performed on a DRON-3 diffractometer with a copper anticathode.

2.4 Determination of the percentage of iron sulfate

Determination of the percentage of iron sulfate iron FeSO_4 (X) is calculated according to the following formula:

$$X = V \cdot 0.1519 \cdot 100 / m$$

where V is exactly 0.1 n quantity. potassium permanganate solution used for titration, ml;
m - mass, g

0.1519 is the amount of ferrous sulfate corresponding to 1 ml of 0.1 N solution of potassium permanganate, g.

The result of the analysis was taken as the arithmetic mean value of three results of parallel determination, the permissible differences between which did not exceed 0.7%. The amount of free sulfuric acid (X1) is calculated by the following formula:

$$X1 = V \cdot 0.0049 \cdot 500 \cdot 100 / m \cdot 250$$

where V is a quantity of exactly 0.1 n. Sodium hydroxide solution for titration, ml; m - sample weight, g;

0.0049 - the amount of sulfuric acid corresponding to 1 ml of sodium hydroxide solution,

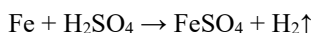
3 Analysis methods of products

The resulting crystals were analyzed for chemical composition using an element analyzer (Regaku Nex DeVS), compound type using X-ray diffraction (XRD), and microstructure using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (JEOL JSM IT 200) analysis. The analysis was carried out at an energy of 30 kV and magnifications of 500, 1000 and 5007 times.

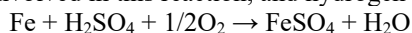
4 Results and discussion

In industry, iron oxide is produced as a by-product in metal working plants, which is obtained when steel products are processed to remove the film from them before further surface treatment [12]. Iron sulfate crystalline hydrate can be isolated from brine solutions by cooling to -5 - 10°C , or by evaporation and then cooling to 20 - 25°C by crystallization [13]. Thus, the main raw material for the production of iron (II) sulfate is iron-containing metal

waste. Dissolving metallic iron in sulfuric acid is a complex process. It was found that the solubility of iron increases up to 50% sulfuric acid solution. A further increase in the concentration of sulfuric acid dramatically reduces the solubility of iron due to the increased oxidizing capacity of the concentrated acid [14]. Therefore, ferrous sulfate is used in the oxidation of starch [15-16]. When iron interacts with sulfuric acid, hydrogen is released:



However, oxygen is also involved in this reaction, and hydrogen is not released as a result:



As can be seen from the above, a complex sequence of reactions can occur in the process of obtaining iron sulfate from industrial waste [17-18]. In order to obtain salts and

other commodity products from industrial waste, it is necessary to develop their processing technology depending on the phase, chemical and granulometric composition of raw materials in each specific case [19]. Based on the research, a synthesis method for producing iron sulfate from waste has been developed. Figure 1 below shows the equipment used to synthesize the iron sulfate from waste.

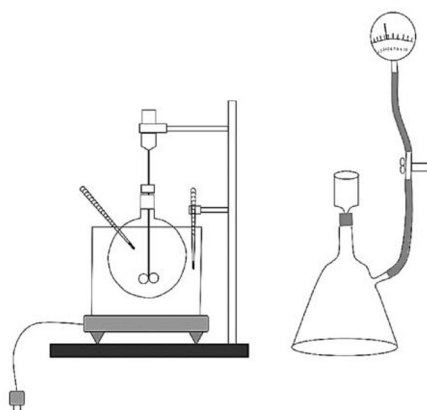


Fig.1. The equipment used to synthesize the iron sulfate from waste

During the procedure, 20 g of crushed and sieved industrial waste containing iron was first placed in a 30% sulfuric acid solution in a flask, the initial acidity of the solution was determined, and the washing process was started. After a certain time, the washing process was stopped, and the resulting solution was filtered in porcelain funnels, washed with a dilute solution of sulfuric acid (1:10), and then washed with distilled water until the residual sulfate ion was removed. After finish the dissolving of wastes in the sulfuric acid some particles of waste not dissolving in solution (super saturated solution). The solution filtered by filter paper, the remaining waste that not dissolved in solution was remain on the paper and the solution passes from it. The color of the solution was sky bluish, as shown in the figure 2.

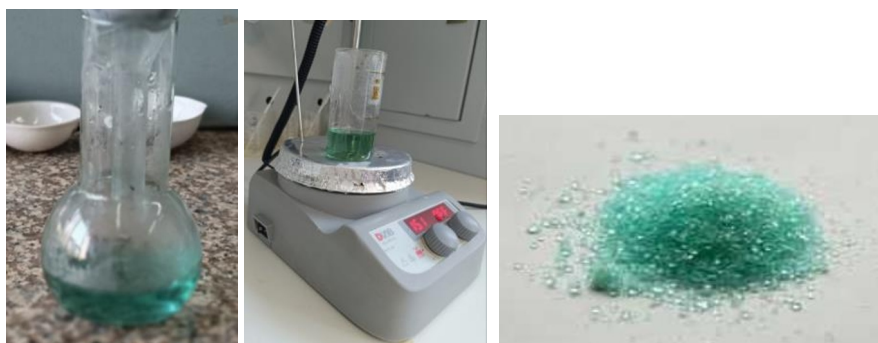


Fig.2. Solutions and final product of ferrous sulfate

The resulting precipitate was dried and analyzed. The content of iron in the filter was also analyzed. Conducting an experiment on leaching of iron from iron-containing industrial metal waste depending on the concentration of sulfuric acid, S:L ratio, temperature, duration (time) of leaching. Figure 3 shows the dependence of the extent of iron leaching from waste on various kinetic parameters.

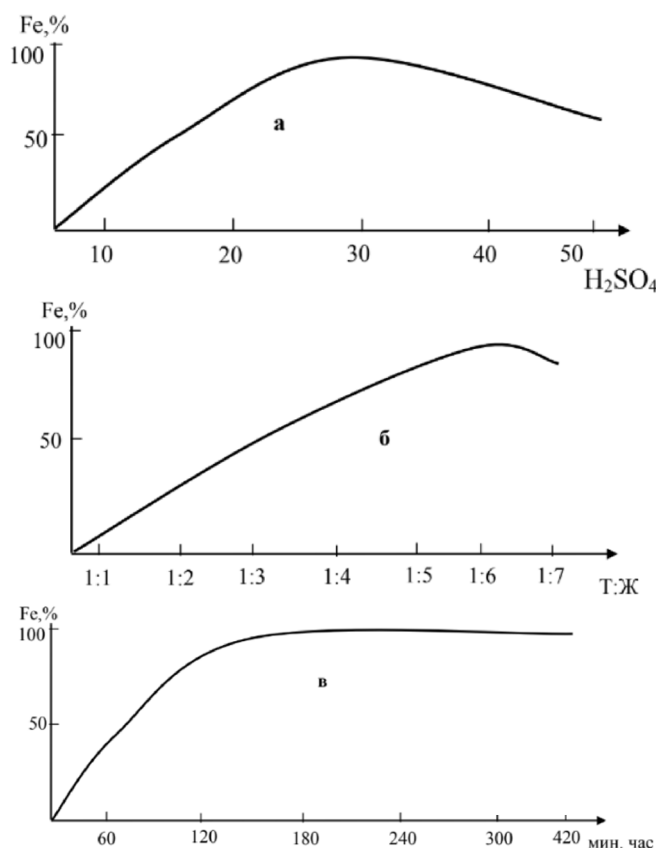


Fig. 3. Dependence of iron leaching rate from waste on H₂SO₄ concentration (a), ratio (b) and leaching time at C[H₂SO₄] = 30% and S:L = 1.

The greatest leaching of iron is observed at a concentration of sulfuric acid of 30% and a ratio of S:L = 1:6. In the first 150-180 minutes, under the above conditions, the level of iron washing increases. Further washing and increasing the acid concentration do not affect the extraction of iron. This is due to the oxidizing properties of concentrated acid and the formation of poorly soluble iron sulfate complexes. Thus, the following optimal conditions for washing iron from slag were found: acid concentration 30%, ratio S:L = 1:6, washing time 150-180 minutes.

Figure 4 shows the dependence of the level of iron leaching from waste on temperature and duration of washing S:L = 1:6, sulfuric acid concentration 30%. It can be seen that the degree of iron leaching depends on temperature and time, and 95-98% of iron passes into the solution.

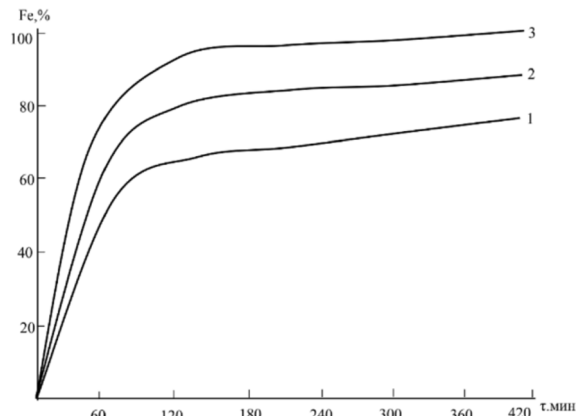


Fig. 4. Dependence of the degree of leaching of iron from waste on temperature and leaching time S:L = 1:6 sulfuric acid concentration 30%, at 1 -333; 2-348; 3-363 K.

The leaching solution resulted in crystallization to obtain ferrous sulfate. Figure 5 shows X-ray images of the initial waste and the iron (II) sulfate formed. It can be seen that after acid treatment, the iron compound in the waste is reduced. The X-ray pattern of the compound obtained after crystallization of the wash solution is consistent with ferrous sulfate [20]. The results shows dominant peaks, of which eight peaks were dominated by iron(II) sulfate and two peaks were dominated by iron(III) sulfate This indicates the presence of iron(II) sulfate minerals under various conditions.

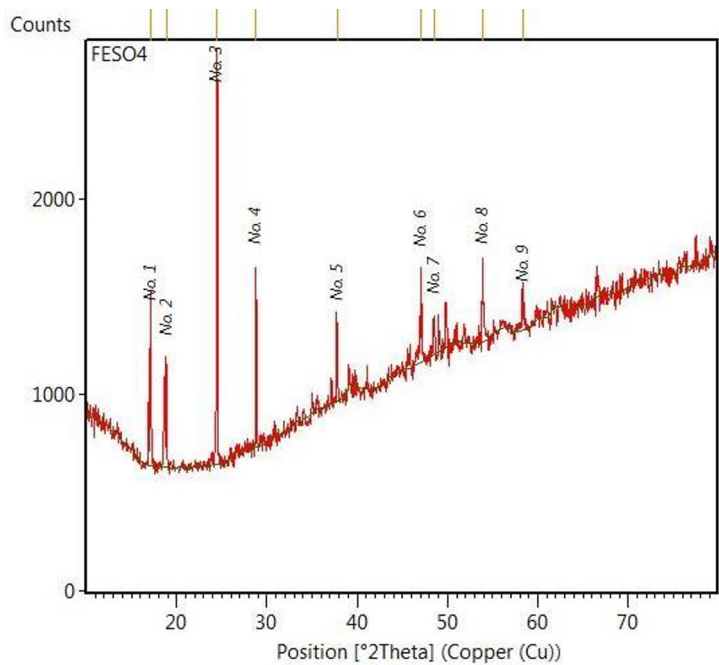


Fig.5. The result of X-ray diffraction analysis of the ferrous sulfate product.

In the IR spectrum (Figure 6) there are absorption bands of sulfate ion at 1149, 615 and water of crystallization at about 1622 cm⁻¹. Based on these data, as well as the results of iron analysis (24-25%), the resulting compound corresponds to the composition of FeSO₄·7H₂O.

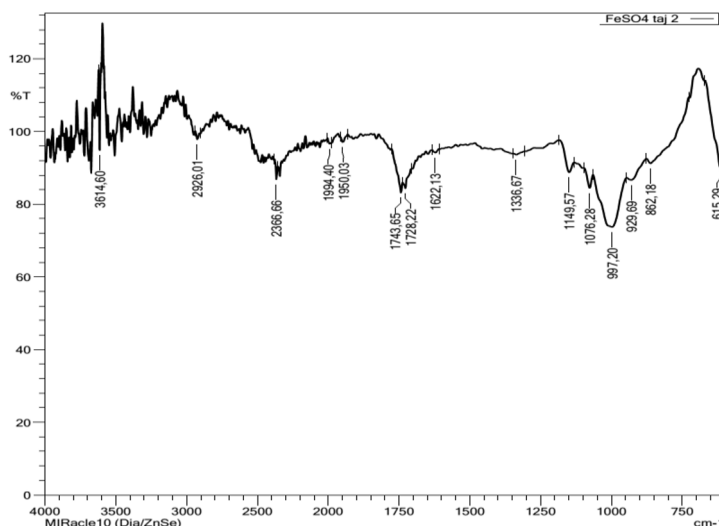


Fig. 6 IR spectrum of sulfate of iron

On average, the ferrous sulfate product contained 27.08% Fe, 58.47% O, 14.45% S and was free of harmful heavy metal elements such as arsenic and lead. The results of this study show that ferrous sulfate can be obtained from scrap metal waste by leaching in 30% sulfuric acid. Found optimal mode for leaching iron-containing metal waste was tested in an enlarged laboratory scale and proposed a basic technology for obtaining iron sulfate vitriol's.

References

1. R Kamble, MG Thakare, AB Ingle. Iron in the environment. Indian J. Environ. Prot 33, 881-888, 2013. 12, 2013.
2. De Mello Gabriel, G.V., Pitombo, L.M., Rosa, L.M.T. et al. The environmental importance of iron speciation in soils: evaluation of classic methodologies. J. Environ Monit Assess, 2021, v.193, p.63.
3. Supplier evaluation on finished goods-relevant products, processes and services Schaeffler group. Calculation principles and rules. Appendix 2 to P 174242 - Issue: Version A 2020-09.
4. Shaked, Y., Erel, Y. and Sukenik, A. The biogeochemical cycle of iron and associated elements in Lake Kinneret. J. Geochimica et Cosmochimica Acta, 2004. v. 68, pp.1439-1451.
5. Erdmann M, Franken G. Sustainability Standard Systems for Mineral Resources. A Comparative Overview – 2022. Bundesanstalt für Geowissenschaften und Rohstoffe. 30.06.2022, revised version 10.12.2022.
6. Policarpo, M. C., & Aguiar, E. C. How self-expressive benefits relate to buying a hybrid car as a green product. Journal of Cleaner Production, 2020. V.252. p.119859.
7. Zhang, S., Ding, Y., Liu, B., & Chang, C. Supply and demand of some critical metals and present status of their recycling in WEEE. Waste Management, 2017. v.5. pp.113–127.

8. Ganor, E., Deutsch, Y. and Foner, H.A. Mineralogical composition and sources of airborne settling particles on Lake Kinneret (The Sea of Galilee), Israel. *Water, Air, and Soil Pollution*, 2000. v.118, pp.245-262.
9. S Sumardi, F R Mufakhir, Y I Supriyatna, W Astuti1, Sudibyo. Processing industrial iron waste into ferrous sulfate as an iron fortification: A preliminary study. *GREENVC* 2021. IOP Conf. Series: Earth and Environmental Science. 2022. v.1017. p.012029.
10. Jankiewicz B., Ptasiński B., Turek A. Spectrophotometric determination of iron (II) in the soil of selected allotment gardens in Łódź. *Pol. J. Environ. Stud.* 2002; 11(6): pp.745-749.
11. Nurchi, V.M.; Cappai, R.; Spano, N.; Sanna, G. A Friendly Complexing Agent for Spectrophotometric Determination of Total Iron. *Molecules* 2021, 26, 3071.
12. Monção R. M., Júnior E. A. A., Bandeira R. M., de Abreu Lima C. D. at all. Evaluation of Corrosion Resistance of Thin Films Formed on AISI 316L Steel by Plasma Using Hastelloy as Cathodic Cage. *Physica Status Solidi (a)*, 2021. 218(10), 2000578.
13. M.F. El-Sherbiny. Crystallization of ferrous sulfate heptahydrate from spent pickle liquor by addition of tertiary butyl alcohol. *Engineering Research- Journal* 2001. Vol 24, No 3. Pp. 101-111.
14. Shaikh, L., Pandit, A., & Ranade, V. Crystallisation of ferrous sulphate heptahydrate: Experiments and modelling. *The Canadian Journal of Chemical Engineering*, 2011. 91(1), pp. 47–53.
15. Sharipov M.S. Study of changes in the properties of starch during oxidation in the creation of a component of adhesive material for surface treatment of paper // *Journal of Chemistry and Technologies*, 2022. v. 30, n.1, pp. 69-78.
16. Tillayeva D., Sharipov M. Starch oxidation and study of changing its properties for use as an adhesive component for the production of corrugated cardboard. *E3S Web of Conf. Volume 402*, 2023 International Scientific Siberian Transport Forum - TransSiberia 2023.
17. Matei E, Predescu AM, Șăulean AA, Râpă M, Sohaciu MG, Coman G, Berbecaru AC, Predescu C, Văju D, Vlad G. Ferrous Industrial Wastes-Valuable Resources for Water and Wastewater Decontamination. *Int J Environ Res Public Health*. 2022 Oct 27;19(21):13951.
18. Wildermuth, E., Stark, H., Friedrich, G., Ebenhöch, F. L., Kühborth, B., Silver, J., & Rituper, R. Iron Compounds. *Ullmann's Encyclopedia of Industrial Chemistry*. 2000.
19. Ahmed M.A. Reusing industrial iron wastes in production of ferrous Sulphate that utilizes in manufacturing of food supplements by selective leaching method. *IOP Conf. Ser.: Earth Environ. Sci.* 2021, 779. pp. 012075.
20. Birhan G. Production, optimization and characterization of iron Sulfate from local iron ore, thesis for the Degree of M.Sc. in Process Engineering., Addis Ababa University Addis Ababa, Ethiopia. 2017, July.