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Fabrication of Ferrous Sulfate from Waste Like Condensed Milk Containing Can and its Characterization

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Abstract

Ferrous sulfate is usually produced from the spent pickling liquor when the metal sheets are pickled in the processing of steel. In the present work ferrous sulfate was prepared by simple acid leaching method by using waste condensed milk can as a raw material. This can contains around 87 percent of iron which was successfully converted to greenish crystals of ferrous sulfate by simple acid leaching followed by crystallization. The process parameters like concentration of acid, molar ratio of iron to acid, period of reaction, effect of temperature and effect of occasional stirring were optimized. Nearly 98% iron was leached out from iron containing can and converted to ferrous sulfate. The product was characterized by chemical analysis, thermo gravimetric analysis and X-ray diffraction analysis. On chemical analysis it was found that the produced product is highly pure, nearly 97 percent. According to the DSC/TGA studies, it is found that the prepared sample is hexahydrate. From X-ray diffraction pattern, it was confirmed that the prepared sample is ferrous sulfate with melanterite phase and have monoclinic crystal structure.

Keywords: Acid leaching; DSC/TGA; Ferrous sulfate; Waste iron; XRD.

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1. Introduction

The commercial name of ferrous sulphate heptahydrate is copperas and represents by the formula $FeSO_4.7H_2O$. Ferrous sulfate heptahydrate is used as chromate reducer for binding harmful chromium compounds in cement or for soil preparation [1]. Significant amount of ferrous sulfate is used for the treatment of waste water and this application is increasing day by day worldwide [2]. Further applications of ferrous sulfate heptahydrate include its use as fertilizer, for phosphate precipitation in purification of sewage water, for conditioning of sewage slurry, for treating iron chlorosis in horticulture, or as raw material for producing iron oxide pigments [1, 3] which is further used in the manufacture of ferrites [4]. It is also used in the manufacture of inks (iron gall ink) and as a mordant in dyeing wool. It has been largely used to control anemia (both in humans and animals) base compound [5-7]. There are two methods for the preparation of copperas in which one is byproduct method and the other is sulfuric acid leaching method [6]. It is mainly produced as the byproduct of TiO_2 manufacture from ilmenite via sulphate process and from steel pickling with sulphuric acid [3]. In sulphuric acid leaching method scrap iron is used for the production of hydrated form of ferrous sulfate [6]. But in the present study the raw material used for the preparation of ferrous sulfate is waste condensed milk can which contains remarkable amount of iron. This paper deals with the preparation of copperas from waste condensed milk can and sulphuric acid. The objective of the present study is to reduce the waste disposal problem as well as to develop a new route for the production of ferrous sulfate heptahydrate. To the best of our knowledge, no such work has so far been reported.

2. Materials and Methods

The waste condensed milk cans were collected from local tea stall. Commercial grade sulphuric acid was collected from the local market. The analytical results of used raw materials and finished product (sample number 23) are given in the table-1.

Table 1: Analytical report of iron waste, sulphuric acid and prepared copperas

	Condense milk containing can									H_2SO_4	Prepared $FeSO_4$
Parameter	Fe	Al	Ca	K	Mn	Sn	Si	PX	NB	purity	purity
Percent	87.63	4.86	2.86	1.64	1.22	1.22	0.60	0.084	0.013	96	96.71

2.1 Fabrication of the product

In this paper, preparation of ferrous sulfate was done in two steps: acid leaching followed by crystallization. At first, the iron content in can chips were leached with sulfuric acid. Before leaching, the raw material was prepared as following way: The collected waste Danish condensed milk cans were properly cleaned, dried and then freed from any organic layer of the surface of the can by slow firing. It was then cut into small pieces and is ready for leaching.

2.2 Experimental Procedure

A fixed quantity of can chips was leached in sulfuric acid in a closed vessel at definite temperature for a certain period. At the end of the leaching period, the leached liquor was separated out, crystalized and recrystallized to get pure product. The resulting product was dried in vacuum drier.

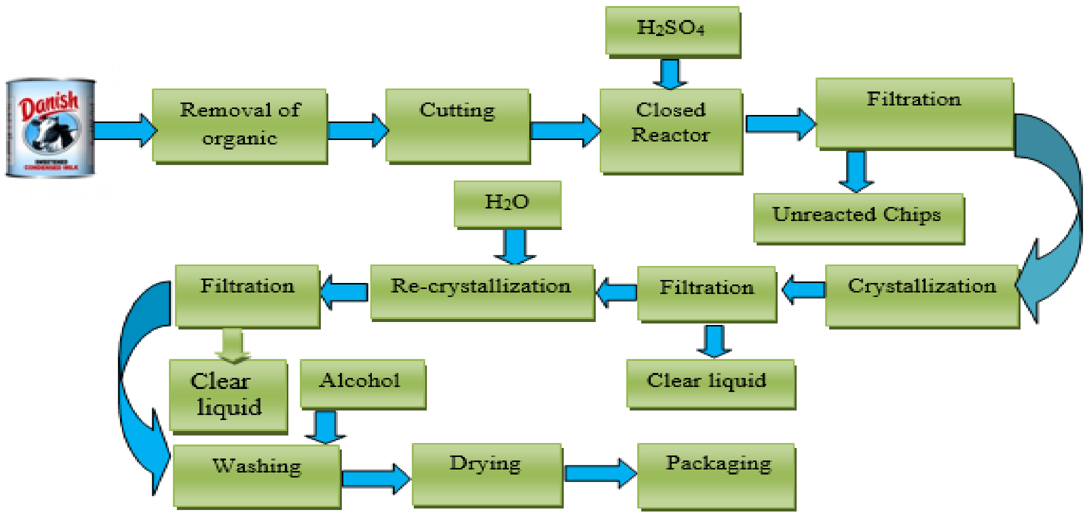

Figure 1: Flow-diagram for the production of ferrous sulphate

There are so many parameters employed during the preparation of ferrous sulfate. Among them concentration of acid, iron-sulfuric acid molar ratio, reaction period, effect of temperature, and effect of occasional stirring on the extent of percent yield are important. A total of 23 samples are prepared by varying above reaction parameters started with about 5.0g can chips. All these products were isolated, dried and analyzed according to the standard procedure.

2.3 Reaction

A replacement reaction takes place during leaching of iron with sulfuric acid as hydrogen is above iron in the reaction series. The reaction is simple, slow and represented as follows:

$$\text{Fe (Can Chips)} + H_2SO_4 \xrightarrow{\Delta} FeSO_4(aq) + H_2(g)\uparrow$$

Crystalisation

$$FeSO_4(aq) \xrightarrow[\Delta]{} FeSO_4.7H_2O\downarrow$$

2.4 EDXRF analysis

Quantitative analyses of the waste can was carried out by EDXRF (Thermoscientific ARL Quant-X).

2.5 Chemical analysis

Chemical analysis of the sample number 23 was carried out according to the standard procedure [8] and the result is shown in the table-1.

2.6 Thermal analysis

The dehydration behavior of sample number 23 was studied by TG and DSC techniques with STA 449 Jupiter thermo analyzer apparatus under dynamic nitrogen atmosphere using an alumina crucible at a heating rate of 10°C/min from 30°C to 650°C.

2.7 X-ray diffraction studies

The phase composition of the prepared copperas was determined by X-ray diffraction analysis by an EMMA diffractometer. The diffraction patterns were recorded using CuKα radiation (λ=1.5406 Å) in the range 10-80 degrees with scanning speed 2 degree/minute. Phase analysis of sample number 23 was performed by comparing the d-values and intensity ratios of the diffraction lines in the recorded patterns with standard data in the PDF file 00-001-0255.

3. Results and discussion

3.1 Process optimization

In the preparation of copperas, effects of different parameters on the extent of yield were studied. Effect of concentration of sulphuric acid on the percent yield are shown in the table-2. Three experiments having acid concentration 0.9375M, 1.8750M and 2.8129M were carried out at 100°C for 11 hours with 7 ml concentrated sulphuric acid in a closed reaction vessel without agitation. Among these three experiments, experiment 2 produces the best result on the extent of yield. The percent yield is calculated as I=[H/B(0.8763×4.976)]×100, where 0.8763 is the conversion factor of iron content in waste beverage can, used as raw material and 4.976 is the conversion factor of iron converted to ferrous sulphate heptahydrate.

Table 2: Effect of concentration of sulphuric acid on percent yield

Exp No. (A)	Amount of Can Chips taken, g (B)	Conc. of H_2SO_4, M (C)	Volume of acid, ml (D)	Unreacted mass, g (E)	Reacted mass, g (F)	Iron content in reacted mass, g (G)	Amount of product, g (H)	% Yield (I)
1	5.0072	0.9375	134.4	0.8085	4.1987	3.6793	17.5106	80.20
2	5.0023	1.8750	67.2	0.0179	4.9844	4.3678	20.7567	95.16
3	5.0333	2.8125	44.8	0.0539	4.9794	4.3634	20.7558	94.57

Conditions: Temperature 100°C, Leaching time 11hr, amount of concentrated acid 7 ml and without agitation

It can observe from table-2 that at lower molar concentration of sulphuric acid (0.9375M), the reaction is not completed though the amount of concentrated acid is same. The percent yield is low (80.20%). At relatively higher molar concentration of acid (1.8750M and 2.8125M), the percent yield is increases but there is a negligible change in percent yield of ferrous sulfate among themselves and for this reason these two molar concentrations (1.8750M, 2.8125M) were selected for further optimization.The effect of molar ratio of iron to acid on the percent yield is shown in table-3. In this series, five experiments were carried out with 1:1.55, 1:1.67, 1:1.78, 1:1.89 and 1:2.03 molar ratio of iron to sulphuric acid in a close reaction system.

Table 3: Effect of molar ratio of iron to sulphuric acid on the percent yield

Exp No. (A)	Amount of Can Chips taken, g (B)	Molar ratio of iron to H_2SO_4 (C)	Unreacted mass, g (E)	Reacted mass, g (F)	Iron content in reacted mass, g (G)	Amount of product, g (H)	% Yield (I)
4	5.0319	1:1.55	0.4308	4.6011	4.0319	19.1599	87.32
5	5.0091	1:1.67	0.0223	4.9867	4.3698	20.7656	95.07
6	5.0333	1:1.78	0.0202	5.0131	4.3929	20.8758	95.11
7	5.0604	1:1.89	0.0190	5.0414	4.4178	20.9936	95.14
8	5.0148	1:2.03	0.0175	4.9973	4.3791	20.8100	95.17

Conditions: Temperature 100°C, Leaching time 11hr, concentration of sulphuric acid 1.875M and without agitation

Table 4: Effect of temperature of reaction on the percent yield

Exp No. (A)	Amount of Can Chips taken, g (B)	Temperature of reaction, °C (C)	Unreacted mass, g (E)	Reacted mass, g (F)	Iron content in reacted mass, g (G)	Amount of product, g (H)	% Yield (I)
09	5.0223	70	0.8040	4.2183	3.6965	17.5660	80.21
10	5.0138	80	0.1359	4.8779	4.2745	20.1157	92.01
11	5.0051	90	0.0859	4.9192	4.3107	20.3099	93.06
12	5.0384	100	0.0512	4.9872	4.3703	20.7680	95.53

Conditions: Leaching time 11hrs, concentration of sulphuric acid 1.875M, molar ratio of iron to acid 1:1.67 and with agitation

It is observed from this table that by using 1:1.55 molar ratio of iron to 1.875M H_2SO_4 the percent yield of ferrous sulfate is 87.32% and maximum yield (95.07%) of ferrous sulfate was obtained by using 1:67 molar ratio. It is also observed that further increasing the molar ratio from 1:1.67 there was no significant change of percent yield of ferrous sulfate and for this reason 1:1.67 molar ratio of iron to sulphuric acid was considered as constant for further optimization. The other leaching condition i.e. temperature, concentration of acid and the leaching period were kept fixed.

Table-4 displays the effect of temperature of reaction on the percent yield of copperas. Four experiments were carried out at temperature 70°C, 80°C, 90°C and 100°C for 11 hr.

It is seen that below 100°C temperature of reaction, the percent yield is low, which indicates that the reaction is not completed. This is because at higher temperature the reactant gain more energy to activate the reaction [8].

Table 5: Effect of period of reaction on the percent yield

Exp No. (A)	Amount of Can Chips taken, g (B)	Conc. of H_2SO_4, M (C)	Period of reaction, hr (D)	Unreacted mass, g (E)	Reacted mass, g (F)	Iron content in reacted mass, g (G)	Amount of product, g (H)	% Yield (I)
13	5.0019	1.8750	10	0.5792	4.4227	3.8756	18.4172	84.44
14	5.0060		11	0.0210	4.9850	4.3683	20.7393	95.01
15	5.0179		12	0.0190	4.9989	4.3805	20.8066	95.09
16	5.0032		13	0.0179	4.9853	4.3686	20.7600	95.16
17	5.0004	2.8125	5.0	0.3437	4.6567	4.0807	19.3916	88.94
18	5.0191		5.5	0.1368	4.8823	4.2784	20.3311	92.90
19	5.0179		6.0	0.0532	4.9647	4.3506	20.6640	94.44
20	5.0098		6.5	0.0227	4.9871	4.3702	20.7474	94.97

Conditions: Temperature 100°C, Leaching time 11hr, amount of concentrated sulphuric acid 7 ml and without agitation

The effect of reaction time for the preparation of ferrous sulfate was studied for both 1.875M and 2.8125M sulphuric acid during the leaching of iron chips and the effects are exposed in the table-5. From table-5 it was observed that the maximum yield of ferrous sulfate was obtained (95.16%) with 1.875M H_2SO_4 and the time required for the leaching was 13 hr. But almost the same percent yield (94.97) was achieved with only 6.5 hr reaction period when the molar concentration of acid was taken 2.8125M.

Table-6 shows the effect of occasional stirring on the percent yield of copperas. Three experiments were carried out with 3.0, 3.5 and 4.0 hr reaction period and it was observed from table-6 that the maximum percent yield was obtained at 4.0 hr reaction period with occasional stirring in an open vessel reactor at 100°C temperature. By occasional stirring the reactant ions are closer to each other causes necessary collision between them and thus the reaction rate increased [9].

Table 6: Effect of occasional stirring on the percent yield

Exp No. (A)	Amount of Can Chips taken, g (B)	Period of reaction, hr (C)	Unreacted mass, g (E)	Reacted mass, g (F)	Iron content in reacted mass, g (G)	Amount of product, g (H)	% Yield (I)
21	5.0349	3.0	0.2184	4.8165	4.2206	18.9023	90.20
22	5.0156	3.5	0.0700	4.9456	4.3338	19.9751	92.60
23	5.0657	4.0	0.0496	5.0161	4.3956	20.2499	93.20

Conditions: Temperature 100°C, Concentration of H_2SO_4 2.8125M, amount of concentrated sulphuric acid 7 ml and with agitation

3.2 Thermal analysis

Figure-2 shows the dehydration behavior of hydrated iron salt (sample number 23) by using DSC and TGA techniques in the temperature interval from 25°C to 650°C in the stem of nitrogen. In the curve TG, there exist four weight loss steps. First weight loss (15.92%) occurs between 63.3°C to 115.0°C temperature which corresponds to the dehydration of two molecules of water. Second dehydration step (weight loss 18.68%) takes place between 116.7°C to 174.9°C, which agrees to dehydration of three molecules of water.

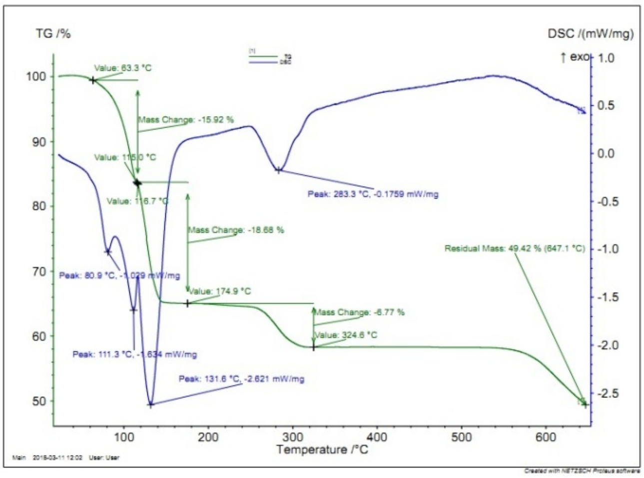

Figure 2: TGA and DSC pattern of prepared copperas

Third weight loss (6.77%) is found between the temperatures 174.9°C to324.6°C which relates to the dehydration of one molecule of water. From this observation, it is found that from temperature 25°C to 325°C the total weight loss is (15.92+18.68+6.77) 41.37 that corresponds to six molecules of water indicating the prepared sample is hexahydrate ferrous sulphate. The final weight loss (9.21) occurs between the temperatures 550°C to 640°C due to the oxidation and sulpher dioxide evolution from the prepared sample.

The DSC thermo grams exhibited the presence of four endothermic peaks at 80.9°C, 111.3°C, 131.6°C and

283.3°C temperature which are slightly higher than those found in the literature [11]. It may be due to the presence of impurities in the sample as well as the sample subjected to carry out DSC/TGA is hexahydrate.

3.3 X-ray diffraction analysis

X-ray diffraction pattern of prepared ferrous sulfate (Sample number-23) and the reference sample of ferrous sulfate (Merck Germany) were shown in figure 3. It can be noted from these two patterns that there exists small shift in the position of the diffraction line. Such shift in the diffraction lines is not unusual in a sample contains some impurities. The additional diffraction lines belong to the impurities. It may be pointed out that on chemical analysis the prepared sample number 23 is found to be around 97 percent pure.

On indexing with data file for copperas (PDF file 00-001-0255), it can seen clearly that most of the diffraction lines corresponds to the melanterite phase with monoclinic crystal structure having lattice parameters a=14.11, b=6.51, c=11.02Å and α=β=γ=105.25 [12]. The diffraction lines which matched well with those reported for the standard sample were from the planes of (-1 0 2), (1 1 1), (-3 1 1), (-4 2 2) and (4 0 4).

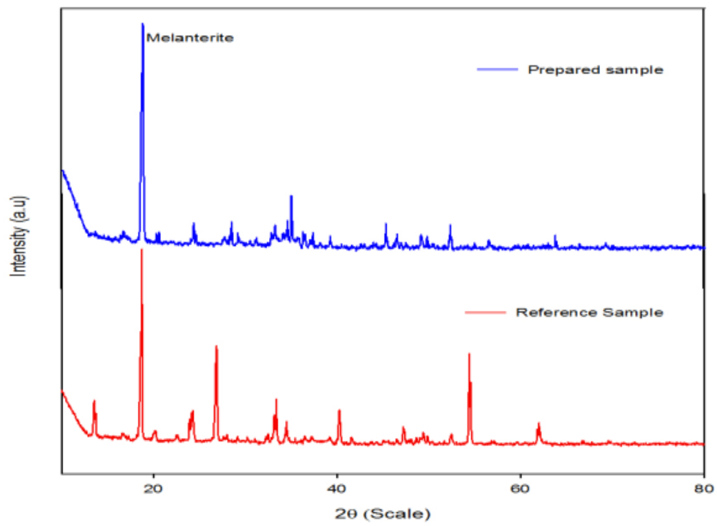

Figure 3: XRD pattern of prepared copperas with reference sample

4. Conclusion

The waste condensed milk pot which contains 87.63% of iron as used as raw material that was successfully converted to bright greenish crystals of ferrous sulfate by simple acid leaching followed by crystallization. In this paper the best result with respect to percent yield and economical point of view, is obtained using 2.8125 M sulphuric acid, 1:1.67 molar ratio of iron to acid, reaction temperature 100°C, reaction period 4.0 hr and with agitation produces 93.20 percent product. On chemical analysis it was found that the produced product is highly pure (96.71%). The prepared ferrous sulphate is hexahydrate found from thermo gravimetric analysis. From X-ray diffraction pattern, it was confirmed that the prepared sample is ferrous sulfate heptahydrate having melanterite phase and monoclinic crystal structure.

5. Recommendation

Purity of the prepared copperas may be increased by further method modification. For the production of ferrous sulfate industrially, pilot plant study is required.

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