CRYSTALLIZATION OF FERROUS SULFATE HEPTAHYDRATE FROM SPENT PICKLE LIQUOR BY ADDITION OF TERTIARY BUTYL ALCOHOL

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ABSTRACT:

Ferrous sulfate heptahydrate (copperas) was recovered by treating spent pickle liquor with tertiary butyl alcohol. Yields of crystallized ferrous sulfate heptahydrate were calculated for different concentrations of liquor at temperature of 25 & 35°C. It is concluded that for the most complete recovery of ferrous sulfate heptahydrate from waste pickle liquor by adding tertiary butyl alcohol, the H_2SO_4 concentration should be as low as possible, the $FeSO_4$ concentration as high as possible, the alcohol to liquor volumetric ratio of 2:1 and temperature of 25°C. For a liquor containing 135 g/l of $FeSO_4$ and 40 g/l of H_2SO_4, the yield was 94.2% using 2:1 volumetric ratio at 25°C.

Key Words: Waste pickle liquor, Pickling of steel, ferrous sulfate heptahydrate (copperas).

Manuscript received from Dr. M.F. El-Sherbiny
Accepted on : 16 / 6 / 2001
Engineering Research Journal Vol 24,No 3, 2001 Minufiya University, Faculty Of Engineering , Shebien El-Kom , Egypt , ISSN 1110-1180

INTRODUCTION:

Steel pickling waste liquors are considered a water pollutant. The recovery of steel pickling waste liquors[1] is one of the main environmental aspects that the steelmaking industry must resolve. There are [2] several processes for the treatment of sulfuric liquors. Continuous recovery of pickle liquors saves acid and reduces waste treatment expenses as well as providing a means of decreasing pickling times.

Acid pickling [3-14] of steel is considered a preliminary chemical process carried out to remove iron oxides from steel surfaces, prior to coating processes such as painting, electroplating, phosphating, enameling etc. Most steel products are pickled using acids such as sulfuric acid, hydrochloric acid, phosphoric acid and hydrofluoric acid. Sulfuric acid has traditionally been the pickling medium for descaling steel. Steel products are treated with a dilute sulfuric acid for a few minutes sufficient to dissolve the surface oxides. The effectiveness of sulfuric acid pickling liquor is reduced as ferrous sulfate is formed. Fresh sulfuric acid must be continuously added to restore the activity of the pickling solution. Over time, the activity of the pickling liquor becomes weak such that it needs to be totally replaced with fresh acid. Waste pickle liquor [15] contains about 134 g/l ferrous sulfate and 33 g/l sulfuric acid.

Previous studied showed that ferrous sulfate was recovered by heating or cooling waste pickle liquors [16-21]. Treatment of waste pickle liquous with acetone [22-26], ethyl alcohol[27], iso-propyl alcohol[28] and 1-propanol[29] were studied to crystallize ferrous sulfate heptahydrate. The object of the present work is to crystallize $FeSO_4.7H_2O$ by addition of tertiary butyl alcohol.

EXPERIMENTAL:

The liquors used throughout this work were prepared by dissolving the required amounts of sulfuric acid and ferrous sulfate hepatahydrate in distilled water. The concentrations studied were 27, 54, 81, 108, 135 and 162g/l ferrous sulfate in presence of 10, 20, 40, 60 and 80 g/l of sulfuric acid. To a certain volume of the liquor tertiary butyl alcohol was added slowly with stirring during addition. The time of addition was about two minutes, the crystallized ferrous sulfate heptahydrate crystals were then filtered. The factors studied which may affect the yield of crystallized ferrous sulfate heptahydrate during crystallization were the concentration of the liquors, tertiary butyl alcohol to liquor volumetric ratio and temperature. The variations in the volumetric ratio of tertiary butyl alcohol to liquor affect the yield of crystallized product ferrous sulfate heptahydrate. The volumetric ratios studied were 1:1, 2:1 and 3:1. Crystallization was carried out at 25 and 35 °C at different concentrations and different volumetric ratios.

After filtration, ferrous sulfate was analyzed to determine its yield and the water content of the crystals. Ferrous and sulfate ions were determined according to standard methods[30]. It was found that water content is seven moles of H_2O per mole of $FeSO_4$ and thus the ferrous sulfate produced was heptahydrate in all experiments. The results of the experiments are shown in figures (1-15)

RESULTS AND DISCUSSION:

Effect of sulfuric acid concentration:-

The results shown in figures (1-14) indicate that the yield of crystallized ferrous sulfate heptahydrate is dependent on the acid concentration. It was found that increasing the acid concentration decreases the yield of $FeSO_4 . 7H_2O$ at constant volumetric ratio, constant ferrous sulfate concentration and constant temperature. For a liquor of 135 g/l $FeSO_4$, using 2:1 volumetric ratio and temperature of 25°C, the percentages of recovery vary in the order 96.2, 95.1 94.2, 92.4 and 91% at acid concentrations of 10, 20 40, 60 and 80 g/l respectively. It is known that waste pickle liquor is removed at about 40 g/l H_2SO_4, so it is practically to crystallize ferrous sulfate at this acid concentration.

It can be concluded that to obtain maximum recovery of ferrous sulfate heptahydrate, liquors of minimum acid concentration must be used.

Effect of ferrous sulfate concentration:-

The results shown in Figures (1-15) indicate that increasing the ferrous sulfate concentration increases the yield of crystallized $FeSO_4.7H_2O$. Using 2:1 volumetric ratio, the percentages of recovery vary in the order 63.2, 80.8, 89.0, 91.4, 94.2 and 95% for liquors of 27, 54, 81, 108, 135 and 162 g/l $FeSO_4$ respectively at 25°C and acid concentration of 40 g/l for all liquors.

It was found that, liquors with low ferrous sulfate concentrations give low yield of crystallized $FeSO_4.7H_2O$. The yield increases sharply, then slightly with increasing of ferrous sulfate concentration. The results show that the percentages of recovery are nearly independent on concentration for high ferrous sulfate concentrations.

Effect of tertiary butyl alcohol to liquor volumetric ratio:-

It is clear from figures (1-15) that, increasing the volumetric ratio increases the recovery of ferrous sulfate hepatahydrate. The increase of volumetric ratio in the order 1:1, 2:1 and 3:1, the percentages of recovery increase in the order 66.9, 94.2 and 96.5% for a liquor of 40 g/l H_2SO_4 and 135 g/l $FeSO_4$ at 25°C. From these results, it is shown that, increasing volumetric ratio from 1:1 to 2:1 increases the percentages of recovery remarkably, but from 2:1 to 3:1 the recovery is increased slightly. The increase of recovery with increasing volumetric ratio may be attributed to the decrease of solubility of ferrous sulfate hepathydrate in the system $(CH_3)_3COH.H_2SO_4.\ FeSO_4.H_2O$.

Effect of temperature:-

It is clear from Figure (13) that increasing the temperature of crystallization decreases the yield of crystallized $FeSO_4.7H_2O$. The decrease at low ferrous sulfate concentrations is greater than that at high concentrations. For liquors of 108 g/l $FeSO_4$ and acid concentrations of 10, 20, 40, 60 and 80 g/l, the percentages of recovery are 95.7, 94,91.3, 89.7 and 88.9% at 25°C, but the percentages are 90.1, 89.2, 86.5, 83.6 and 80.5% at 35°C using volumetric ratio of 2:1. Because of the waste pickle liquor is removed at about 140 g/l ferrous sulfate, the suitable temperature for crystallization of $FeSO_4.\ 7H_2O$ is 25°C.

CONCLUSION:

From the previous discussion of results, the recommended conditions for crystallization of ferrous sulfate heptahydrate using tertiary butyl alcohol are:-

1- Ferrous sulfate concentration between 135 and 162 g/l.

2- Sulfuric acid concentration between 20 and 40 g/l.

3- Tertiary butyl alcohol to liquor volumetric ratio of 2:1.

4- Temperature of 25°C.

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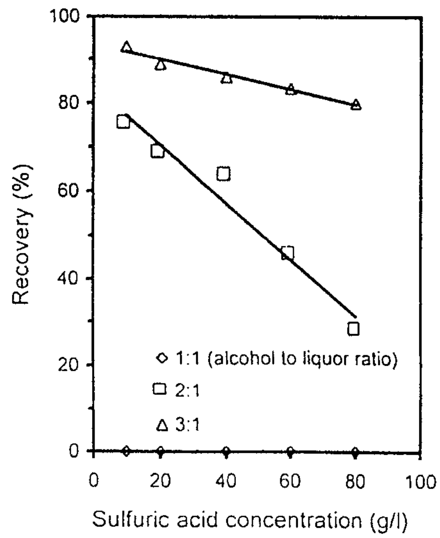

Fig. (1): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 27 g/l
Temperature :25°C

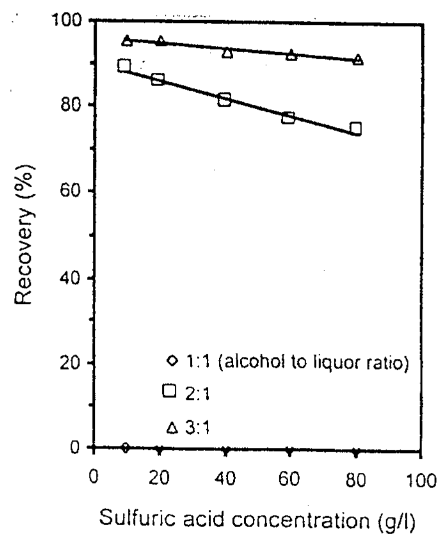

Fig. (2): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 54 g/l
Temperature :25°C

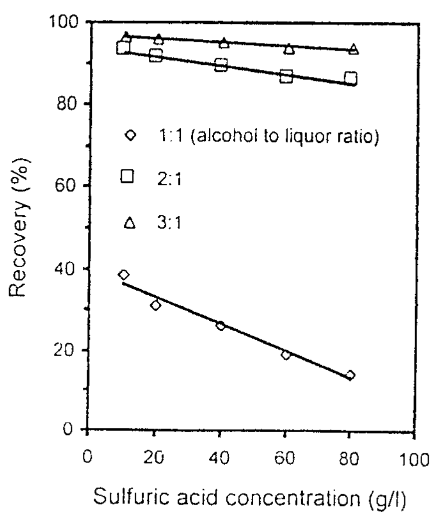

Fig. (3): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 81 g/l
Temperature :25°C

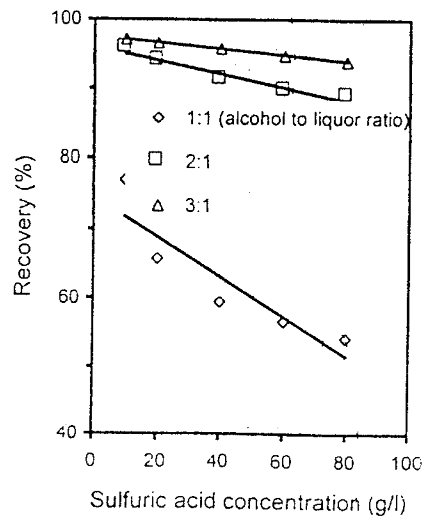

Fig. (4): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 108 g/l
Temperature :25°C

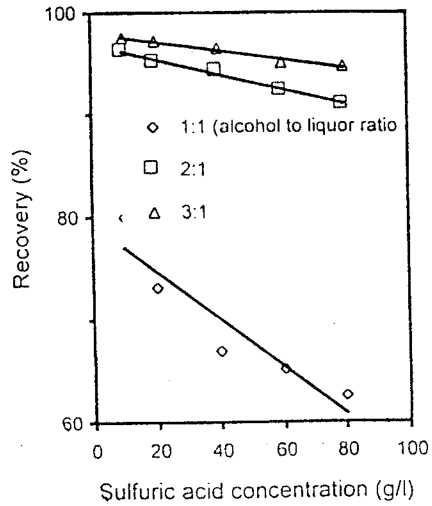

Fig. (5): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 135 g/l
Temperature :25°C

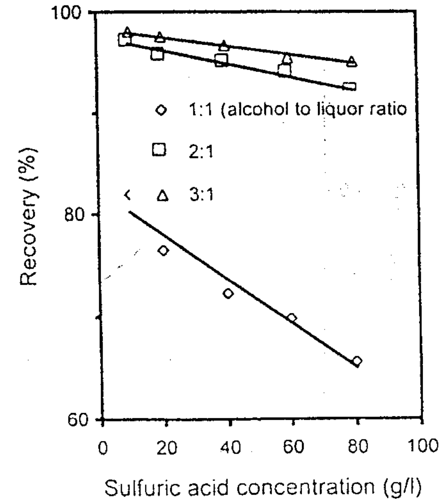

Fig. (6): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 162 g/l
Temperature :25°C

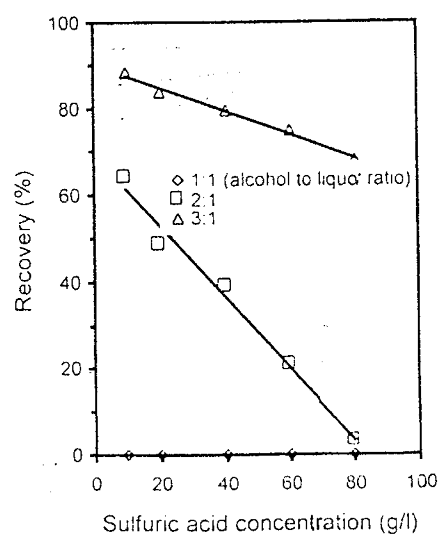

Fig. (7): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 27 g/l
Temperature :35°C

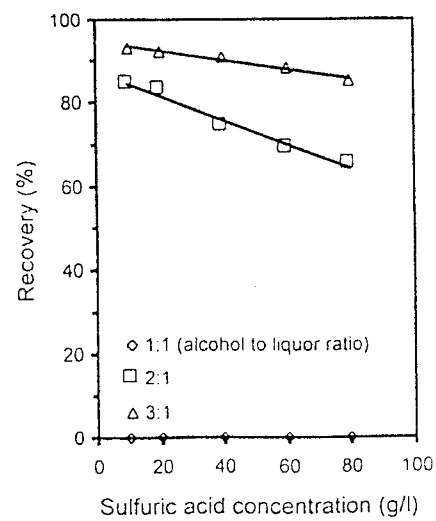

Fig. (8): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 54 g/l
Temperature :35°C

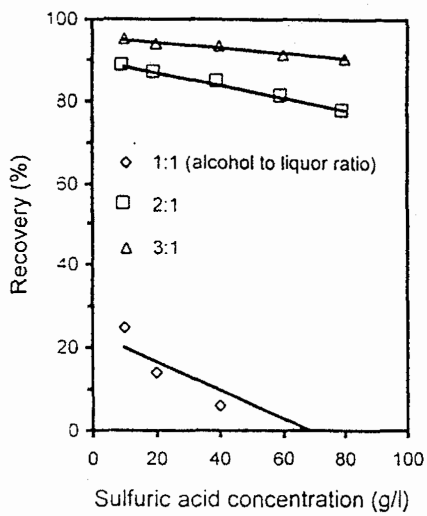

Fig. (9): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 81 g/l
Temperature :35°C

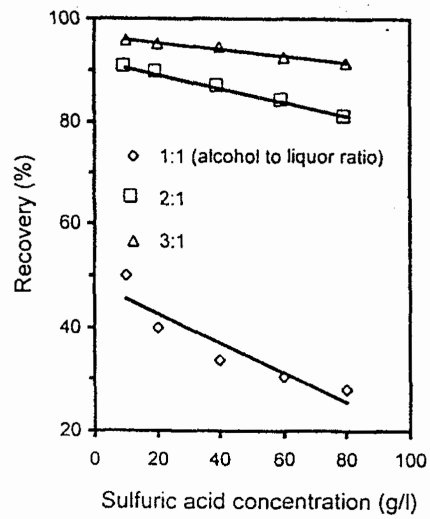

Fig. (10): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 108 g/l
Temperature :35°C

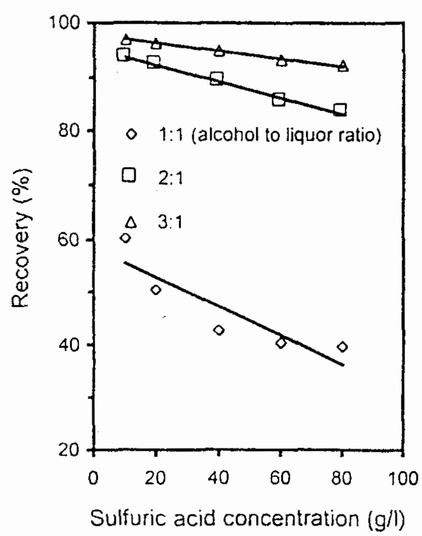

Fig. (11): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 135 g/l
Temperature :35°C

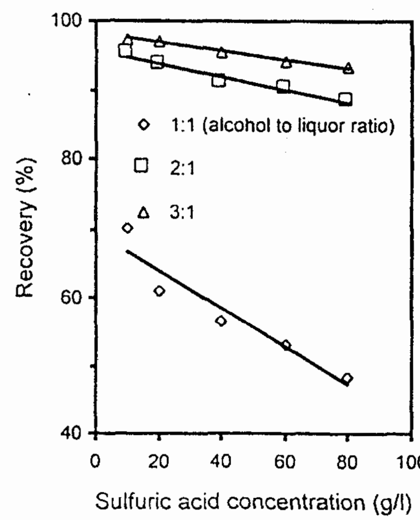

Fig. (12): Effect of concentration of sulfuric acid and tertiary butyl alcohol to liquor volumetric ratio on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 162 g/l
Temperature :35°C

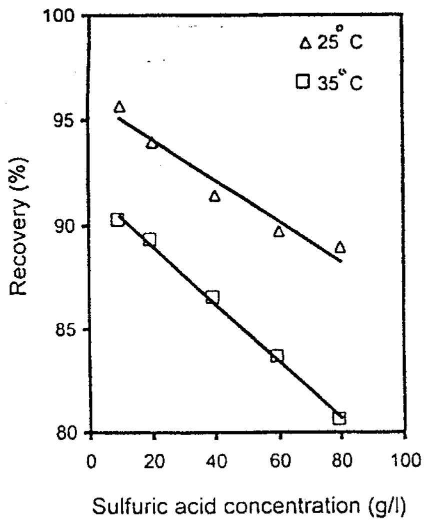

Fig. (13): Effect of concentration of sulfuric acid and temperature on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 108 g/l
Tertiary butyl alcohol to liquor ratio: 2:1

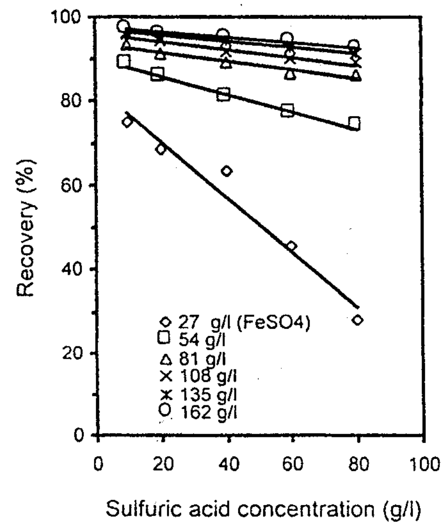

Fig. (14): Effect of concentration of sulfuric acid on recovery of ferrous sulfate heptahydrate at different ferrous sulfate concentrations.
Conditions:
Tertiary butyl alcohol to liquor ratio: 2:1
Temperature :25°C

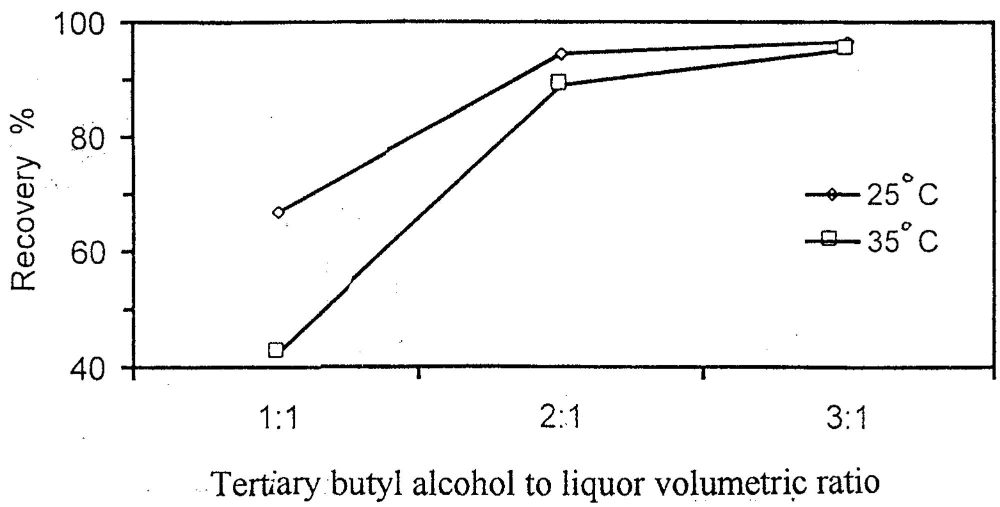

Fig. (15): Effect of tertiary butyl alcohol to liquor volumetric ratio and temperature on recovery of ferrous sulfate heptahydrate.
Conditions:
Ferrous sulfate conc. : 135 g/l
Sulfuric acid conc. : 40 g/l

بلورة كبريتات الحديدوز سباعية الماء من مخلف
تخليل الصلب باضافة الكحول البيوتيلى الثلثى

محمد فتحي الشربيني

قسم العلوم الأساسية الهندسية ــ كلية الهندسة ــ جامعة المنوفية

- تم استرجاع كبريتات الحديدوز سباعية الماء بمعالجة مخلف تخليل الصلب بالكحول البيوتيلى الثلثى ، وتم حساب نسب الإستخلاص لكبريتات الحديدوز سباعية الماء عند درجتي حرارة ٢٥ ، ٣٥ °م باستخدام تركيزات مختلفة من حامض الكبريتيك وكبريتات الحديدوز ، وكذلك نسب حجمية مختلفة من الكحول البيوتيلى الثلثى إلي المحلول.
- ويوصى بأن يكون تركيز الحامض أقل ما يمكن ويكون تركيز كبريتات الحديدوز أعلى ما يمكن وإستخدام نسبة حجمية ١:٢ من الكحول إلى المحلول وكذلك درجة حرارة ٢٥ °م.
- وبتطبيق هذه التوصيات على محلول تركيزه ٤٠ جم/لتر من حامض الكبريتيك ، ١٣٥ جم/لتر من كبريتات الحديدوز وبإستخدام نسبة حجمية ١:٢ أمكن إسترجاع ٢ر٩٤% من كبريتات الحديدوز سباعية الماء عند ٢٥ °م.