

Dec. 8, 1942.

H. E. KEYES

2,304,178

SULPHATING PROCESS AND APPARATUS THEREFOR

Filed May 15, 1939

3 Sheets-Sheet 1

FIG. 1.

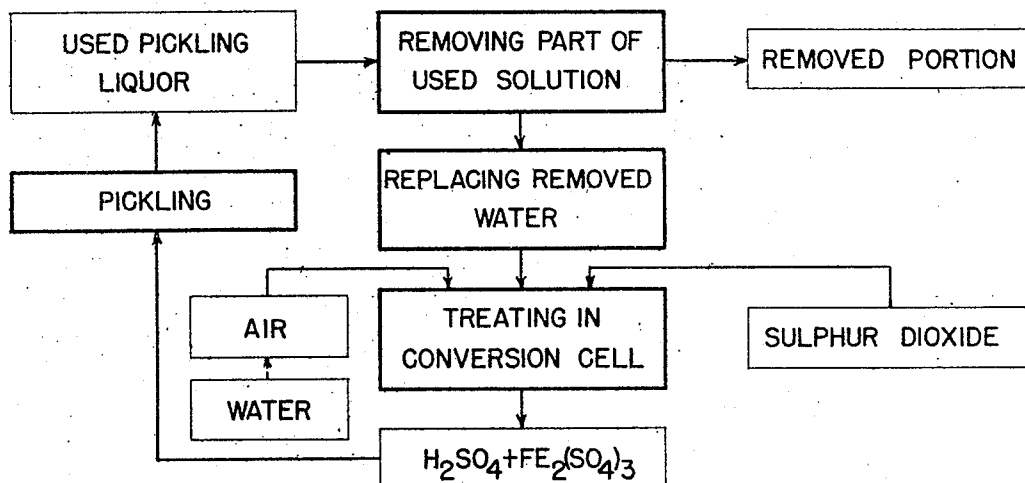
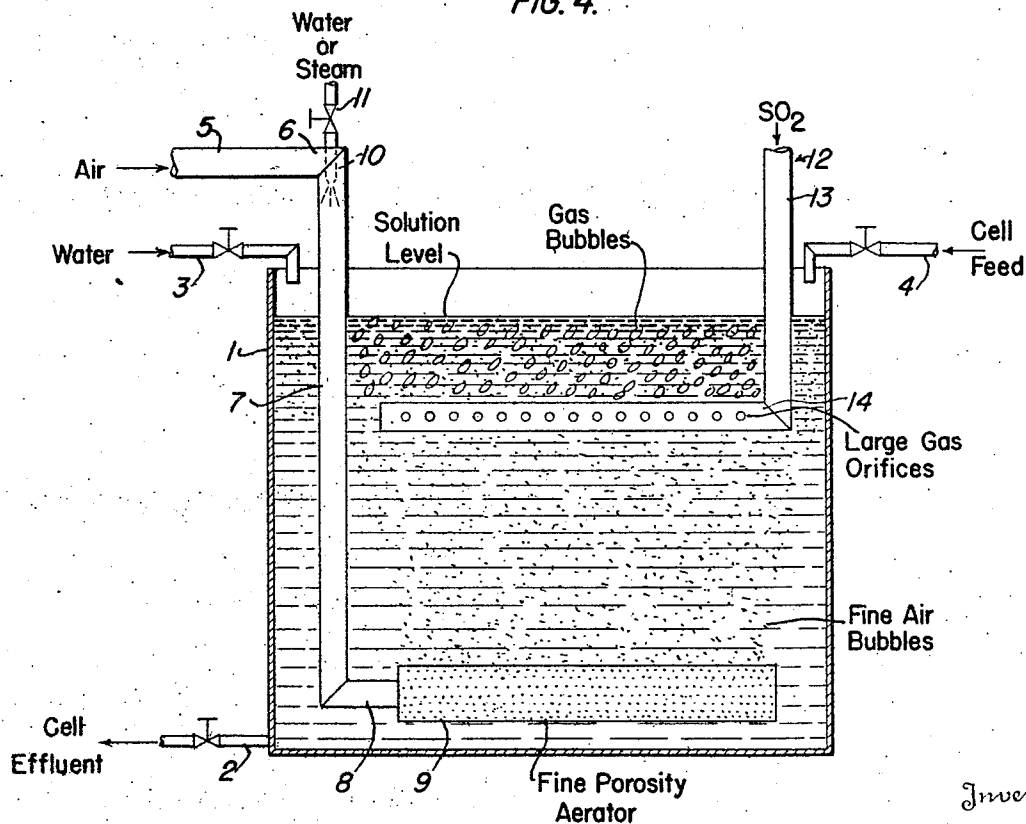


FIG. 4.



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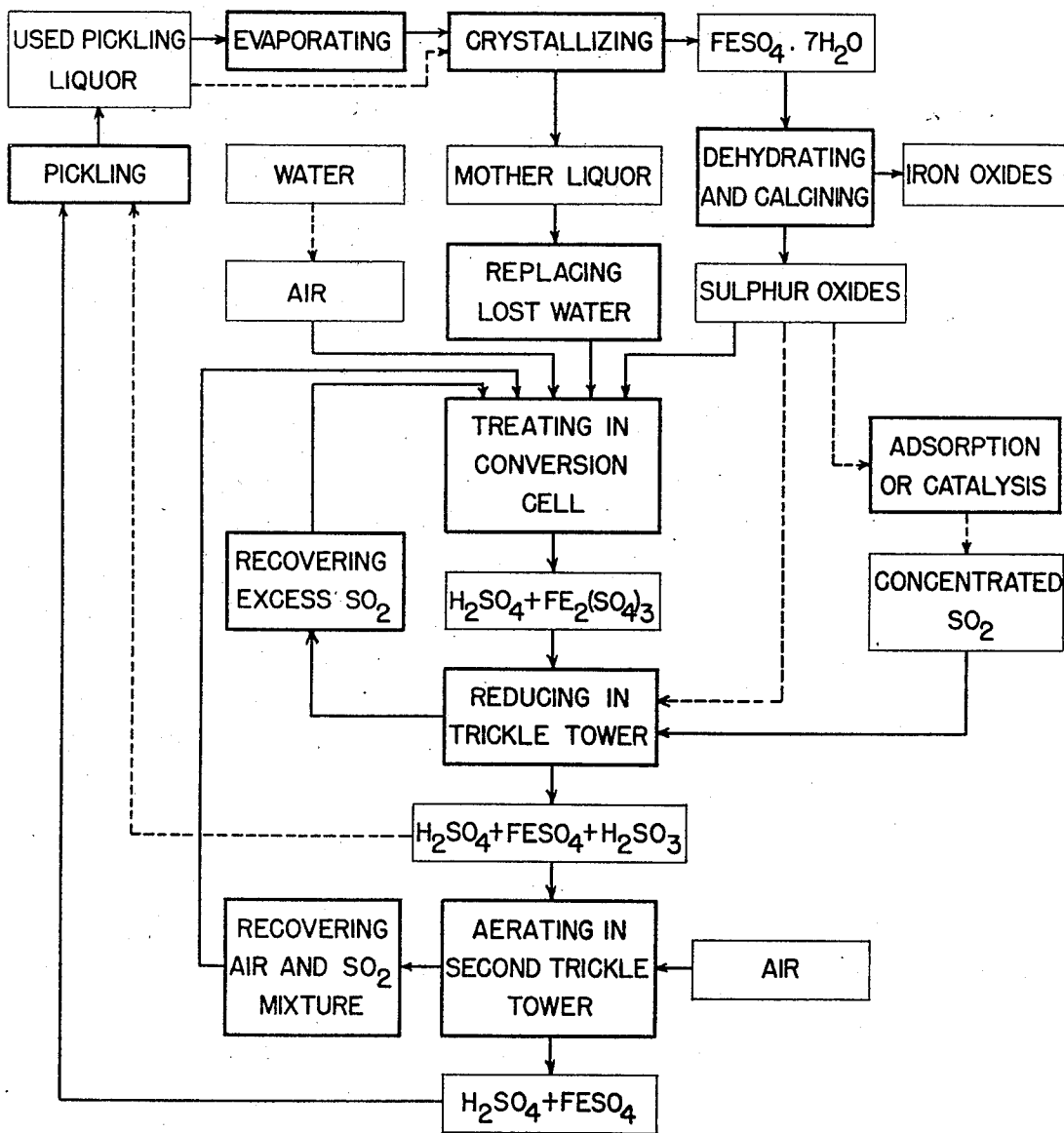
2,304,178

SULPHATING PROCESS AND APPARATUS THEREFOR

Filed May 15, 1939

3 Sheets-Sheet 2

FIG. 2.



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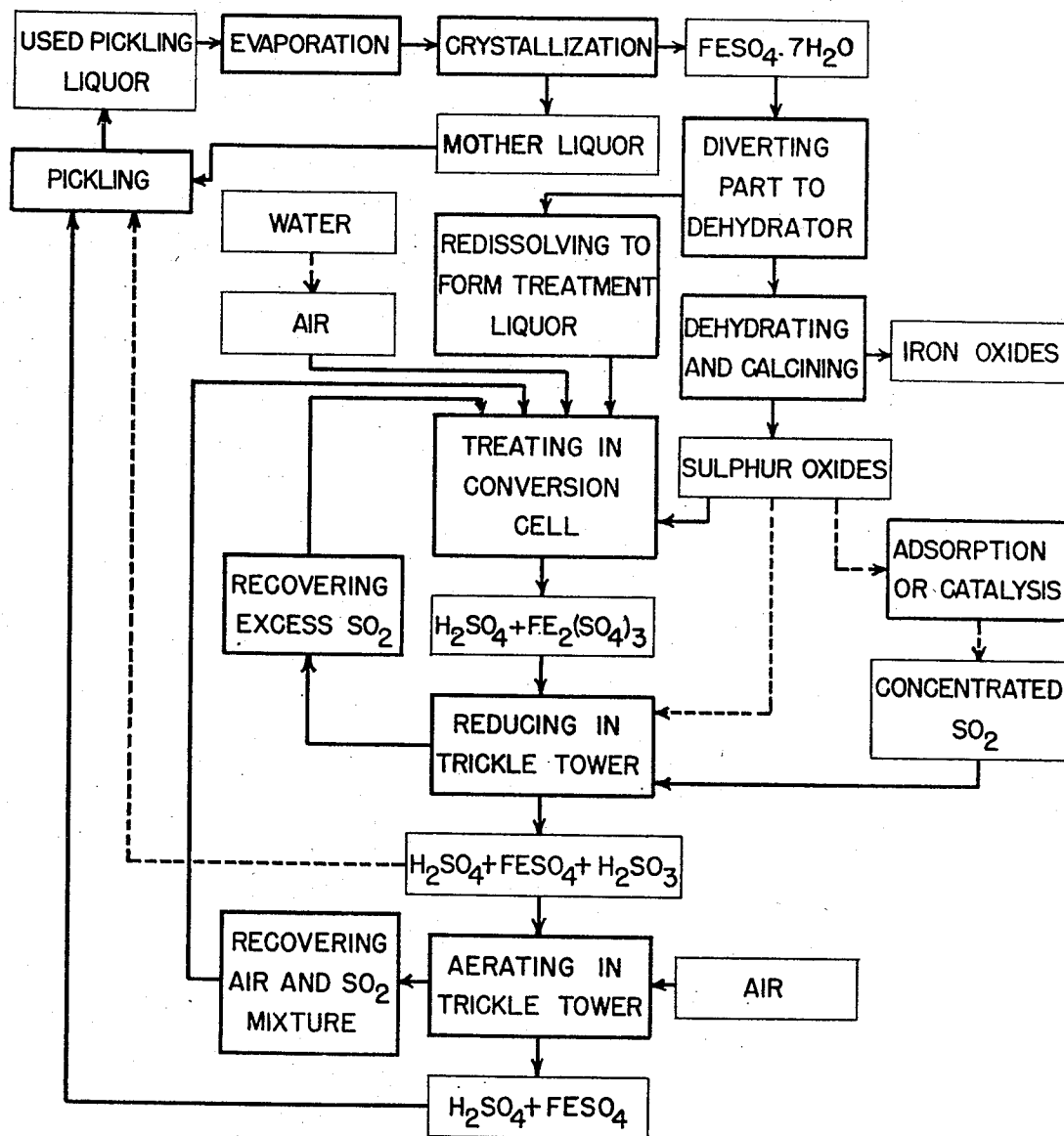
2,304,178

SULPHATING PROCESS AND APPARATUS THEREFOR

Filed May 15, 1939

3 Sheets-Sheet 3

FIG. 3.



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2,304,178

SULPHATING PROCESS AND APPARATUS THEREFOR

Harmon E. Keyes, Phoenix, Ariz.

Application May 15, 1939, Serial No. 273,791

12 Claims. (Cl. 148—8)

My invention relates to the production of acid type solutions for steel pickling and to apparatus adapted therefor. More particularly, the present invention is concerned with sulphuric acid pickling solutions and their regeneration in closed circuit.

This application is a continuation in part of and an improvement upon my copending application Serial No. 241,023, filed November 17, 1938.

Formerly in the acid pickling of iron and steel, it has been the practice to use a bath of 100 grams of sulphuric acid per liter prepared on the spot from concentrated sulphuric acid. As the pickling process is carried out, it depletes the acid content of the pickling bath and builds up a ferrous sulphate content, dissolving iron scale together with some iron.

To compensate for loss of effectiveness due to pickling, the treatment liquor was, in the past, fortified with more concentrated sulphuric acid. The pickling solution was discarded when the dissolved iron content reached about 50 grams per liter and the free acid content fell to values ranging around 10 to 50 grams per liter.

The former use of concentrated sulphuric acid and the wastage of pickling liquors added needlessly to the cost of producing iron and steel. It has been estimated that 500,000,000 gallons of such pickling liquors have been wasted annually. Also, this wastage was generally dumped into streams and legislation increasingly restricts this practice. Consequently there is a need for reclamation of waste pickling liquors or their conversion to by-products.

My improved process, has, as one of its objects, the overcoming of the above outlined difficulties.

Another object of my invention is to regenerate spent pickling liquor by lessening the metal content without permanently removing the associated sulphate materials.

Another object of my invention is to produce from pickle liquor useful by-products, particularly ferric sulphate solution at any desired pH or iron strength, and for any purpose, such as previously disclosed in my above co-pending application.

A further object of my invention is to regenerate spent pickling liquor by crystallizing ferrous sulphate from the pickling liquor, replacing the water content thus removed and passing sulphur dioxide and air through the resulting solution to exert a sulphating action.

Another object of my invention is to main-

tain a substantially closed system for the regeneration of pickling liquor.

Still another object of my invention is to decompose the removed ferrous sulphate for the recovery of oxides of sulphur, more cheaply than by standard acid production.

Yet another object of my invention is to increase the sulphuric acid concentration of spent pickling liquor by converting a metal sulphate solution to a sulphate of a higher order of oxidation and then reducing the solution with sulphur dioxide.

A still further object of my invention is to provide a conversion cell for converting sulphur dioxide into sulphate form as ferric sulphate directly upon entry into an aqueous solution containing enough iron salts to be useful in a pickling tank employing ferric sulphate.

With these and other objects of my invention which may be apparent from the specification, my invention resides in the subject matter now set forth.

Briefly, the present invention comprises several methods of catalytically sulphating a spent steel-pickling solution by forming sulphuric acid in the solution or changing certain metal sulphate from a lower state of oxidation to a higher one. The invention also comprises a conversion cell adapted to facilitate the above methods by enabling sulphur dioxide and air to react in the solution with sulphating effect.

In some modifications of my process, the sulphated regenerated pickling liquor from the conversion cell is reduced with sulphur dioxide to increase the maximum sulphuric acid concentration that can be produced by this type of process. In this way, the presence of iron in the spent pickling solution is an advantage instead of being a handicap. Because iron salts exist in two states of oxidation, the ferric state of the solution can be used as a means of oxidizing sulphur dioxide and combining with water to form sulphuric acid.

One modification of my process involves diverting a small portion of waste pickle liquor to the regeneration cell where, by addition of water, air and SO₂, acid suitable for pickling is produced.

In some modifications of my process, excess ferrous sulphate is removed from the pickling vat effluent by crystallization, and the mother liquor is sent through the conversion cell. The removed ferrous sulphate is decomposed to yield sulphur dioxide for the conversion cell and the reduction treatment.

In other modifications of my invention, after crystallization of ferrous sulphate, the mother liquor is recirculated to the pickling tank. A part of the ferrous sulphate is redissolved and sent to the regenerative treatment in substantially acid-free condition. After being regenerated the solution is used to fortify the mother liquor sent back to the pickling vat.

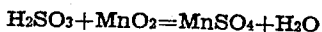
In cases where return of spent liquor is objectionable in pickling, my cyclic process is carried out by complete evaporation of the acidic ferrous sulphate solution, calcining of the acid bearing ferrous sulphate and reclaiming of the sulphur oxides as herein described.

The cell treatment referred to embraces the general principles embodied in the "autoxidation" method as described in my copending application Serial No. 241,023. As pointed out in the above application, formation of acid in the conversion cell takes place in the presence of iron salts after oxidation of the iron to ferric form has become practically complete. Other criteria for efficient oxidation set forth in the above application are hereby made a part of this specification.

It is further disclosed as a part of this invention that metal salts in solution, other than iron, may be employed in my process for producing pickling acid by contacting SO₂ and air with solution. This may be desirable in order to avoid loading of the system with iron salts and also to avoid presence of ferric sulphate at any point in the system. Examples of such metal salt catalysts that may be dissolved in the sulphate solution are manganese, nickel, chromium, molybdenum or vanadium. Inasmuch as such metals are used in certain alloy steels, these sulphates may in some cases become ingredients in pickling solutions and may thus be diverted to the acid regeneration cell. If desired, manganese oxide ore may be leached by sulphurous acid for this purpose. Manganese may be employed catalytically at lower concentrations than iron, and may be preferable for that reason, in certain cases. Also, manganese salts do not require reduction. Each of the metal salt catalysts that I may use in producing pickling acid may have its own peculiar advantage for a specific purpose.

Because of its catalytic action at low concentrations and its ability to function at higher acid strengths than in the case of iron, manganese may be usefully employed as in the method shown by Figure 2 in which acid is built up in a solution already relatively high in acid and low in iron. In such cases acid may be generated without substantial oxidation of iron, thereby eliminating necessity for iron reduction as well as permitting acid generation in a solution so high in initial acid that iron will not oxidize satisfactorily.

A further advantage of manganese lies in the fact that in cyclic pickling small concentrations of manganese as here employed may not crystallize out with the iron so that only a negligible quantity need be added at each cycle. Such additions may be conveniently and almost automatically accomplished by recirculating acid cell solution through a bed of manganese oxide ore so that the contained sulphurous acid may leach the manganese according to the reaction.



If the solution becomes deficient in manganese the sulphurous acid content will increase due to lack of conversion of SO₂ which will then leach more manganese and thereby lower the H₂SO₃ in the solution. The total rate of dissolution of

manganese and, therefore, the manganese content of the cell solution is governed by the rate of solution circulation through the bed of manganese ore. Any other convenient source of manganese may, of course, be used.

In order to assist the understanding of my invention, I have included three accompanying flow diagrams, Figures 1, 2 and 3, to be considered with the specification as illustrative of my process. Figure 4 depicts the preferred form of my conversion cell and is made a part of this specification.

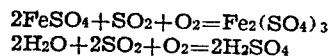
The size of the portion of liquor retained in the circuit is determined by the concentration of iron salts desired in the pickling solution. The bulk of spent pickling liquor is discarded or treated as a by-product such as later described. A volume of water equal to that removed is added to the remaining liquor in the circuit, preferably as feed to the conversion cell and the liquor passed into the conversion cell to be brought up to that acid strength necessary for effective pickling.

I do not wish to be limited to employment of any specific type of sulphur dioxide conversion apparatus as long as similar results in the process as a whole are obtained, and as long as conversion of sulphur dioxide to sulphate form takes place directly in the solution containing metal salt catalyst which is to be regenerated for use in pickling. However, the conversion cell as described in this and my related copending application Serial No. 241,023, filed November 17, 1938, is preferred. I have found this type of cell to contribute considerably, through its efficiency, to the successful results obtained. Successful results are secured in spite of high concentrations of iron as well as residual acid in the cell feed.

In the conversion cell as here preferred, sulphur dioxide and air are introduced into the liquor, as by blowers. The air is introduced near the bottom of the conversion cell, its entry being in the form of fine bubbles encountering substantial compression by the liquid. Nearer the surface by hydrostatic pressure of the liquid, sulphur dioxide is introduced in the form of large bubbles. This conversion cell is described in detail later in the specification.

Sulphur dioxide may be derived from the roasting of pyrite or the calcining of ferrous sulphate. Sulphur dioxide may be secured by burning sulphur, in which case a pressure type burner may eliminate the need of a blower for the sulphur dioxide.

Conversion of sulphur dioxide to sulphate and sulphuric acid, which takes place in the conversion cell depends upon the thorough admixture of air and solution which takes place below the zone of sulphur dioxide entry. The diluted, spent pickling liquor, which contains residual sulphuric acid and also ferrous sulphate, is increased in acid content and the ferrous sulphate is oxidized to the ferric form. The following equations represent the reactions:



The ferrous sulphate liquor discarded as described above may be advantageously applied for water or sewage treatment according to the method disclosed in my copending application, the copperas solution containing free acid usually being first treated with scrap iron to neutralize acid and dissolve more iron. The neutral ferrous

sulphate solution is then applied in the manner described in the copending specification.

The modification as shown in Figure 2 provides for the selective crystallization of a large part of the ferrous sulphate. This enables a removal of excessive iron in the pickling solution without removing the sulphuric acid with it. Pickling liquor is used hot in scaling iron and steel, sometimes being used at a temperature of 200° Fahrenheit. By concentrating and cooling the pickling-vat effluent, much of the ferrous sulphate can be removed. Even in the absence of sulphuric acid which lowers the solubility of the ferrous sulphate, saturation values are of the following order for ferrous iron.

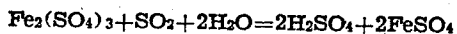
Temperature °C.....	0°	10°	20°	60°
Fe" gm. per liter.....	55	75	95	200

Concentrating and cooling may be accomplished in a number of ways as illustrated by evaporation, trickling, water cooling, aeration by blowing, refrigeration and their combinations.

After the crystallization step just described, the mother liquor, containing residual acid and ferrous sulphate, is sent to the conversion cell of the same type as already described. However, manganese may be added so that higher acid strength may be permitted. As in the modification shown by Figures 2 and 3, water that has been lost to the circuit must be replaced. Preferably this is done by adding water to the cell feed. In case crystallization was by cooling alone, no water need be added.

Following treatment in the sulphur dioxide conversion cell, the treated liquor is passed to a trickle tower where sulphur dioxide is passed countercurrent to the downward trickle of liquor. This trickle tower treatment takes place without addition of excess air as distinguished from the conversion cell treatment, thus introducing sulphur dioxide under reducing conditions.

By means of reduction of ferric sulphate with sulphur dioxide in the reducing trickle tower, more sulphuric acid is formed. The equation can be stated as follows:



Also in this manner the Fe:H₂SO₄ ratio in the regenerated pickling liquor can be regulated.

I have discovered that, contrary to the generally accepted theory of reduction of ferric iron by SO₂, reduction does not take place ordinarily to more than a slight extent even with pure SO₂ in presence of acid of the strength required for pickling, but that by the special modification as here disclosed reduction is rapid and complete from ferric to ferrous iron even employing SO₂ of the ordinary strength resulting from calcining ferrous sulphate or burning sulphur. This is accomplished by concentration of the SO₂ upon an adsorbent and either simultaneously or subsequently passing the ferric sulphate solution through the said adsorbent whereupon the ferric iron is quickly and completely reduced. The preferred method of reduction is to trickle the ferric sulphate solution through a bed of granular activated carbon past the upward moving current of SO₂ containing gas. This may be otherwise accomplished as by bubbling the gas into a body of the solution containing carbon in suspension. Lamp black or other forms of carbon may be used more or less effectively in either form of apparatus. By countercurrent trickling through activated carbon, a substantial temperature increase is obtained which is of advantage in that the re-

duction was found by experiment to proceed more rapidly with increase in temperature. This is of further advantage in coordinating the entire process in that the SO₂ cell reaction is also exothermic so that the combined effect of both the oxidizing and reducing stages is to heat the acid solutions automatically to a suitable temperature for pickling. This heating effect is further enhanced, as compared to former attempts to apply this autoxidation process, by virtue of the greater efficiency of the SO₂ conversion cell here described. Preheating of pickling solution by steam is thus minimized.

Inasmuch as this adsorption effect of carbon for SO₂ may come under the realm of catalysis, it is the aim of this disclosure to include any substance which may catalyze the reduction of ferric iron by SO₂.

Likewise, I may employ an adsorbent, catalyzer or promoter in the oxidation stage, providing that such has a selective effect for increasing the activity of oxygen instead of SO₂.

My preferred procedure is to first completely oxidize the iron from a substantially neutral solution, then to build up acid at a high rate until about 70 gm. per liter H₂SO₄ is formed, then to complete the acid cell reaction at a lower rate commensurate with the satisfactory conversion of SO₂, and finally to completely reduce the ferric back to ferrous iron by SO₂ and the aid of an adsorbent. These separate and distinct steps may be conducted by either batch or continuous type operation by single or multiple stage.

While, in the normal operation of the sulphur dioxide conversion cell, the iron will preferably become largely oxidized to ferric sulphate for optimum cell operation such a completion of oxidation is not necessarily critical to successful results. By continuing the conversion cell operation to produce the maximum feasible acid strength, say 100-150 grams per liter with the iron still largely oxidized, and by then contacting this cell solution with relatively strong sulphur dioxide and without finely disseminated air, acid is produced at a higher concentration than otherwise possible. Thus, 1 gram Fe in being reduced produces 1.76 grams H₂SO₄, so that if 60 grams per liter ferric iron is so reduced 105.6 grams equivalent acid is produced. If the acid in the cell effluent has been raised to 100 grams per liter the final strength is then 205.6 grams H₂SO₄ per liter, a figure twice as high as is generally feasible by direct conversion. This type of conversion cell operation gives a means of producing a satisfactory acid to use in modern continuous strip picklers which employ an initial acid concentration of over 150 grams per liter.

In operating the reduction tower to produce a maximum quantity of acid there will be an excess of sulphur dioxide which will pass through the tower. This excess gas is collected and passed into the conversion cell as by a suitable blower.

By sending the strong sulphur dioxide from the roasters or sulphur burner first through the reducing tower and then to the sulphate conversion cell, the strong reducing power of the gas is used to best advantage, after which the remaining sulphur dioxide is absorbed and converted from a lower concentration to give a very complete utilization, the high and low concentrations of the sulphur dioxide being logically utilized in the reducing and oxidizing sections of the circuit in that order.

After treatment in the reducing tower considerable sulphur dioxide remains in the liquor

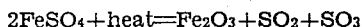
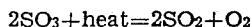
in the form of sulphurous acid unless the solution is nearly boiling. In some cases, sulphurous acid may have a beneficial action in pickling, particularly in presence of considerable dissolved iron, as H_2SO_3 in solution would tend to counteract the sluggish effect of high iron concentration by supplying additional acid without increasing the sulphate content.

When the sulphur dioxide content of the acid solution is desired to be held at a lower figure than that in the reduction chamber effluent, the solution is passed through a second trickle tower or aeration tower which displaces the sulphur dioxide by aeration, the evolved gas combining if desired with that from the first tower and fed through a blower into the conversion cell. The fact that the sulphur dioxide scrubbed from the aeration tower is mixed with air is not an objection. This gas can be introduced into the conversion cell through the normal sulphur dioxide pipe.

Crystallized ferrous sulphate is removed in the present process from the mother liquor in the form having seven molecules of water of crystallization. This $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is dehydrated preferably at low temperature to approximate the composition $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ after which the material is calcined at such temperature and concentration of reducing agent that the evolved gas contains a satisfactory ratio of $\text{SO}_2:\text{SO}_3$. In my process an appreciable concentration of SO_3 does no harm and may be beneficial in that by the method of gas absorption here employed SO_3 is beneficially utilized. The furnace may attain temperatures up to 1000°C ., under controlled condition of gaseous atmosphere contacting the charge, which makes possible a considerable dissociation of sulphur trioxide to sulphur dioxide.

The degree of SO_3 absorption may be greatly increased by passing the gas through a porous medium which will serve as a filter to extract and absorb the SO_3 existing as a fine sulphuric acid mist and which is thus added to the cell solution as by passing moisture through or onto the porous medium. Thus, the necessity of adding a reducing agent to reduce SO_3 and form objectionable carbon monoxide in the calcining step may be practically eliminated.

Thus by calcining the removed ferrous sulphate, it is decomposed into ferric oxide and sulphur trioxide, sulphur dioxide and oxygen. The following equations are illustrative:



Sulphur oxides produced from the decomposition of the ferrous sulphate are thus available to supply the sulphur dioxide conversion cell. Theoretically, the oxides of sulphur would remain entirely within a closed system and there would be no need for any additional sulphur dioxide to be added. However, a certain amount of SO_2 from an outside source is necessary to make up the deficiency caused by various losses. This may be supplied by a sulphur burner or from calcining additional copperas or from any other material that will furnish sulphur dioxide. This gas is either added to the reducing trickle tower as shown or to the conversion cell. Sulphur dioxide resulting from the calcining is added to the cell by suitable means preferably a blower.

The iron oxide resulting from the calcining operation may be used as paint pigment or reduced to metallic iron. In the latter case, it may be suitable for a blast furnace charge, but

as an improvement on such practice I propose to employ a calcining kiln in a separate step and with additional reducing agent for conversion to sponge iron which can be utilized as such or melted directly into steel.

In the modification shown in Figure 3, a portion of the crystallized copperas is dissolved to produce a conversion cell feed at any desired iron concentration but without appreciable residual acid. Such solution after passing through the cell and being given the required reducing sulphur dioxide treatment is then added to the pickling circuit at any desired point. In other words, instead of running the mother liquor through a regenerative treatment in the conversion cell, most of it is recirculated directly back to the pickling vat. In cyclic pickling, the solution additions such as those attributable to redissolving crystallized ferrous sulphate, are of course balanced in volume by withdrawal of an equal amount of solution or water from any point in the circuit by any means applicable to the process. For example, withdrawal may be made by more evaporation and prior to the crystallization step. Or the mother liquor may be evaporated while being heated for use in pickling, or a portion of the mother liquor may be diverted to form by-products. This mode of operation offers the advantage that by adding neutral solution to the conversion cell a greater net production of free acid in the cell effluent results than by feeding to the cell a solution containing appreciable free acid.

A given sized conversion cell and trickle tower installation can thus maintain a greater volume of pickling. The modification of Figure 3 permits a return solution, from the regenerative treatment, of higher acid strength than could be handled in the sulphur dioxide conversion cell.

If desired, the method according to either Figure 2 or Figure 3 may be conducted by withdrawing a portion of the pickling effluent prior to evaporation or crystallization for the conversion cell feed according to the modification shown in Figure 1. In certain cases the pickling effluent is largely wasted or used for various purposes outside the SO_2 cell circuit, in which event only a small proportion is diverted to the SO_2 cell, as shown in Figure 1.

As a variation of the process described in Figure 3, the effluent from the conversion cell may be returned to the pickling vat without further sulphur dioxide treatment. By varying the conditions of conversion cell operation as taught by my copending application, Serial No. 241,023, the acid content of cell effluent may be controlled. Since the cell feed is derived from redissolved ferrous sulphate residual acid is at a minimum.

The above process may be used to produce ferric sulphate at any desired acidity and for any purpose, inasmuch as neutral crystallized copperas may be added to the cell feed and acid inhibition in the resulting ferric sulphate accomplished to any desired extent. Also, pickling tank effluent containing free acid may be similarly employed by first contacting with metallic iron or other acid reacting substance to neutralize free acid, thereby simultaneously increasing the iron content of the solution or producing some other desired reaction.

In such operation of the SO_2 conversion cell as may involve a controlled pH during the iron oxidation, I have found it beneficial to conduct such iron oxidation in presence of a comparatively small amount of iron hydrate so that any free

acid forming tendency is automatically counteracted by reaction with iron hydrate as well as sulphite formation avoided, thus affording a means of effecting a greater sulphur conversion capacity of the cell by both acid and sulphite inhibition and also of applying such practice to pickling solution oxidation.

It is recognized in the art that ferric sulphate has advantages in certain types of pickling, such as stainless steel. It has been the custom to add anhydrous ferric sulphate for this purpose, which material may not only cost ten times as much as ferric sulphate produced by my method, but also the pickling systems have additional burden of more iron to unload sooner or later, which condition is relieved by my method of producing ferric sulphate from iron already in the system. Electrolytic pickling, now favored for stainless steel, may be accomplished to advantage by aid of ferric sulphate which may eliminate expensive nitric acid formerly employed.

As shown in Figure 4, the conversion cell comprises, in my preferred form, a tank 1 having an outlet pipe 2. A water inlet pipe 3 and a cell-feed inlet pipe 4 are placed at the top of tank 1.

Extending down into the tank 1 at one side of it is air conduit 5, having an elbow 6 at the top, a straight piece 7 extending downward therefrom and a second elbow 8 joined to piece 7. A porous tube 9, closed at one end, is positioned horizontally near the bottom of tank 1. Tube 9 is joined at its open end to nipple 8, preferably by means of a resilient sleeve or bushing in which latter case the nipple fits inside the tube. Placed in upper elbow 6 is a jet 10 aligned with the bore of straight piece 7. Jet 10 is controlled by valve 11 above elbow 6 and is adapted to inject and admix a regulated amount of steam, water, or solvent into the flow of air through air conduit 5.

At the opposite side of cell 1 is a sulphur dioxide conduit 12, having a vertical straight piece 13 extended down below the solution level. Joined on to the straight piece 13 is a horizontal perforated piece 14 having its free end sealed.

As to the preferred conversion cell construction advocated for the process, it should be noted that sulphur dioxide gas is added at relatively low pressure a short distance beneath the solution surface, the apertures in the sulphur dioxide conduit 12 being of sufficient size to avoid clogging by dust in the gas. In contradistinction the aeration tube 9 is of a permeability to produce very fine air bubbles, preferably of 1 mm. diameter or less, and is so located as to aerate the whole of the solution. The convenient depth of the tank 1 may be between 3 to 15 feet.

It is contemplated for either plan of operation to employ a centrifugal type blower of suitable construction to withstand the gas at the temperature employed and suitable pressure characteristics to introduce the sulphur dioxide gas under a head solution of 1-3 feet by means of a perforated pipe which entire system may be so designed as to enable handling large amounts of dust in the gas without clogging. Accumulations of dust in the sulphur dioxide blower and distribution system may be eliminated by internal sprays which sluice the material and discharge it either into the conversion cell or by suitable traps away from the cell. In special cases where pure sulphur is burned the blower may be eliminated by use of a pressure type sulphur burner.

The air to the conversion cell is separately introduced preferably at the bottom of the cell and through porous aerators to subdivide the air to

the required degree and thus effect oxidation of SO_2 and ferrous iron. Thus, the sulphur dioxide is introduced at low pressures, as 1 to 3 lbs. per sq. inch, and as large bubbles through orifices of a size not to be clogged by fine dust, whereas the air is introduced at a greater submergence, higher pressures, such as 5 to 10 lbs., and with an extremely fine state of subdivision. The air, being cleaned if necessary, is thus supplied in a finely divided condition and at uniform pressure.

The pressure of the sulphur dioxide, and, therefore, its concentration and rate of addition, and the resultant cell operation are likewise maintained constant by the relatively large apertures through which the sulphur dioxide is discharged into the cell solution.

I have found that when aerating solutions through fine porous media such as may here be employed for air a tendency to clogging may occur from causes within the solution itself. This may take place when the solution is nearly saturated with either a highly soluble or a slightly soluble substance or when very fine solid particles are present in suspension. Apparently the forces of capillarity, crystallization and turbulence around the orifices pull solution containing solids in solution or suspension into the pores during aeration and the vapor pressure of the liquid in contact with the air at these points causes a local drying effect, thereby depositing solids within the pores of the medium during aeration.

It is disclosed as a part of this invention pertaining to the aeration features to counteract any such clogging tendency and thus maintain the porosity of an aerator by introducing a small stream, spray or mist of water or solvent material into the pipes or ducts leading to the porous medium, thereby keeping the porous medium moist and thus dissolving or washing out of the pores material from suspension or solution. This moist condition of the porous medium also inhibits the original deposition of solid material in the pores. This water or solvent is added to travel concurrently with the air through the porous medium, thus keeping the medium saturated by this spray introduced with the air so that liquid from the main body is prevented from permeating the pores.

This prevention of clogging of porous aerators as here disclosed is applicable to water or sewage aeration, ore flotation using porous mats or any other industry employing fine dissemination of gas into solutions by means of porous media that ordinarily tend to clog. The cause and prevention of clogging was demonstrated experimentally by aerating through alundum thimbles into a sulphuric acid solution saturated with calcium sulphate. In 23 hours, the pressure rose 2.24 inches of mercury. By adding a slow stream of water intermittently into the air pipe the pressure dropped 0.6 inch of mercury in $2\frac{1}{2}$ hours and by similarly adding a small quantity of NaCl as solvent for CaSO_4 the pressure in two hours more dropped to the original value. This was further demonstrated experimentally by similarly aerating a soluble sulphate solution containing considerable ferric hydroxide in suspension. Before precipitating the iron the aerators operated 6 hours at a substantially constant pressure of 5 inches of mercury. After 8 hours further operation with the iron precipitated the pressure rose to 16 inches of mercury and was still rising when dilute acid was introduced into the air line which lowered the pressure to nearly its original value.

By maintaining a water film over the surfaces

of the aerator pores the pore space may be decreased, thereby affording means of producing finer air bubbles than normally possible with a given permeability aerator. This gives further insurance against clogging of aerators by making possible use of coarser rated aerators for the same bubble size.

When operating the cell with very strong iron solutions an improved result is possible by maintaining the cell operation at that concentration of acid which gives greatest capacity, which may be 30-50 gm. acid per liter, the acidity then being increased to 100-200 gm. per liter by separate reduction of the ferric iron with strong SO_2 . By continuous rather than batch operation of the cell, conditions are maintained for optimum operation of the conversion cell.

The iron concentration of the SO_2 cell solution is of any convenient concentration, but preferably above 1.5 grams per liter so that the $\text{Fe}^{+++}:\text{H}_2\text{SO}_4$ ratio of the SO_2 cell solution is of the proper order to produce a solution suitable for pickling conditions. In modern continuous strip pickling systems, the free acid in the effluent may be 40 grams per liter or more, the Fe in solution being approximately 50 to 100 grams per liter, thus furnishing to the SO_2 conversion cell a feed containing higher acid and iron than anticipated in former practice with the autoxidization process. It is the aim in the present method to send to the conversion cell, pickling effluent of any reasonable concentration of iron or acid as well as various chemical agents used as inhibitors to corrosion in the pickling tank. This furnishes a different type of cell operation in that relatively high strength of acid is produced in presence of a high concentration of iron.

Examples of conversion cell operation illustrate the types of flow sheets. The plan of Figure 1 is shown by a test with iron at 4.8 gm. per liter and no initial acid, results being shown below.

Hours run	To distribution SO_2			Soln., gm. per liter		Rate, gm. per liter per hr.
	Fe^{+++}	H_2SO_4	Lost	Fe^{+++}	H_2SO_4	
9.0.....	4.0	93.2	2.8	4.6	97.5	10.85
13.0.....	2.4	80.2	17.4	4.1	121.5	9.35

In both cases above the air was added at the rate of 0.75 cubic foot per minute per cubic ft. solution volume and the ingoing gas contained 4.0 volume percent SO_2 .

A similar run, but with iron 50 gm. per liter, gave a rate of acid formation of 10 gm. per liter per hour at practically 100 per cent SO_2 conversion, the iron becoming completely oxidized, this conversion efficiency being effective over a range of acid strength up to about 77 gm. per liter, the acid being brought to a final strength of 132 gm. per liter with a drop to about 90 percent SO_2 conversion at the end of the run.

When employing metallic salts catalysts in small concentrations such as iron at less than 5 gm. per liter or manganese or other salts at less than 1 gm. per liter, even with a very fine aerator the bubbles almost immediately coalesce so that the benefit of the fine dissemination of air is not obtained. It is the aim of this process to inhibit this coalescence, in other words to effectively aerate solutions through a reasonable portion of the column height with air maintained in the originally fine state of dissemination, and thus secure with very low concentration of metal salt

catalyst the same type of effective results that have been obtained with high iron concentration. It is found that this inhibition of coalescence automatically occurs at high iron concentration, but that for low metal salt concentration an agent must be added to inhibit coalescence. This agent may be one of many known substances that produce a tenacious surface film which does not break on coincidence of bubbles, of which pine oil is an example. The combination of initially fine bubbles, adequate degree of aeration and inhibition of coalescence together give the requisite condition for successful cell operation and this effect is evidenced by a definite froth column on top of the cell liquid and which may be from 5-20 per cent of the entire solution column height. As an example, the cell was operated with only 1 gm. per liter manganese as sulphate, the initially fine bubbles from the alundum aerators almost immediately coalescing to many times the original size. After adding 4 drops of pine oil to the charge of solution of 12 liters the solution became milky as a result of the dissemination of fine bubbles and the loss of SO_2 from the cell dropped as a result to about a tenth of the value before adding the inhibitor. Also, it was noted that froth to a depth of one-half inch appeared on top of the solution and remained as long as the inhibitor existed in the proper concentration, which was an indication of proper cell operation as no froth existed at this low manganese concentration until the inhibitor was added.

Manganese sulphate has been found satisfactory in lieu of iron catalyst for producing pickling acid. A test run with 1 gm. Mn per liter as sulphate, as above, produced acid at the rate of 2 per cent per hour up to 10 per cent strength, the rate of acid formation not falling off appreciably until 10 per cent strength was reached, as compared to 5 per cent acid when iron was used as catalyst. The run with manganese was continued at a somewhat reduced rate of SO_2 for 16 hours, the final acid strength being 25.2 per cent, thus giving a suitable pickling acid without any iron content.

Using any desired strength SO_2 , and separately adding finely divided air, complete oxidation of iron is obtained and without forming any free acid unless desired, by maintaining a small amount of an acid consuming substance, such as iron hydrate, in suspension in the solution. Prior to treatment with SO_2 pickle liquor may be first neutralized with any alkaline substance if final acidity is not desired. This gives conditions for maximum cell capacity and minimum loss of SO_2 .

Regarding the field of application of my process it may be used for either vat or strip pickling of iron or steel and various other alloys preferably those with an iron base. Other metal sulphates which will exist in two states of oxidation may be used in the conversion cell the metal salts acting catalytically in the process in some cases without actually being converted into the higher state of oxidation.

It will be seen that my process provides a relatively simple means of absorbing the sulfate portion of pickling salts back into the steel plants by conversion to acid without the costly equipment characteristic of standard acid production. Also ferric sulphate of any desired concentration may be produced and applied as an adjunct to sulphuric acid, in the pickling operation. This ferric sulphate, being produced from

by-product ferrous sulphate, does not cause an additional amount of iron to be discarded as is the case when standard ferric salts from an outside source are added. In the regeneration cell, sulphur dioxide of any convenient strength may be employed.

It will also be seen that I have provided a means for increasing the pickling activity of used pickling solutions in continuous or batch operation by removing ferrous sulphate and introducing air and sulphur dioxide into the used pickling solution. Sulphur dioxide may be secured from any source available including gases derived from calcining the removed ferrous sulphate.

Manifestly my process of utilizing in the conversion cell sulfur oxides produces by calcining or roasting is of particular advantage as not being stopped by carry over of undesirable materials. This process is particularly distinguished from the contact acid process in that initial SO_3 does not need to be removed or reduced, but can be directly absorbed in conjunction with the SO_2 in the cell as by passing the gas into the cell through a coarse porous medium and injecting preferably a water spray concurrently with the gas through the coarse medium and into the acid solution system. Furthermore, only partial gas cleaning is required.

Also, it is manifest that by employing high strength iron in the regeneration cell feed and by continuously operating the conversion cell at an acid strength corresponding to the maximum capacity for sulphur conversion and then reducing the ferric sulphate with strong sulphur dioxide to produce additional free acid, a stronger acid strength and greater cell capacity is obtained than possibly by using low iron concentrations or a single step conversion.

While I have shown for the purposes of illustration specific embodiments of my invention, it will be understood that various changes may be made in the treatments, steps, forms and proportions without exceeding the scope or spirit of my invention, and that I am to be limited only by the scope of my invention and the appended claims.

I claim:

1. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include treating the spent liquor to divide ferrous sulphate contained therein into two portions of which one portion is in solid form and the other is in aqueous solution; calcining the solid ferrous sulphate to produce a gas containing SO_2 ; introducing air and said SO_2 into said solution of ferrous sulphate to promote conversion of the SO_2 to a sulphate radical, the air and SO_2 being introduced in amounts sufficient to form sulphuric acid in the solution and thereby produce a regenerated sulphuric acid solution for use in pickling liquor.

2. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include crystallizing ferrous sulphate out of the spent liquor; redissolving in water a part of the crystallized ferrous sulphate to form a solution; calcining the remainder of the ferrous sulphate to produce a gas containing SO_2 ; introducing air and said SO_2 into said solution of ferrous sulphate to promote conversion of the SO_2 to a sulphate radical, the air and SO_2

being introduced in amounts sufficient to form sulphuric acid in the solution and thereby produce a regenerated sulphuric acid solution for use in pickling liquor.

3. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include treating the spent liquor to divide ferrous sulphate contained therein into two portions of which one portion is in solid form and the other is in aqueous solution; calcining the solid ferrous sulphate to produce SO_2 and SO_3 ; separating out SO_3 by combining with water to form sulphuric acid; introducing air and said SO_2 into said solution of ferrous sulphate to promote conversion of the SO_2 to a sulphate radical, the SO_2 and air being introduced in amounts sufficient to form sulphuric acid in the solution and thereby produce a regenerated sulphuric acid solution for use in pickling liquor.

4. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include evaporating the major portion of the spent liquor to substantial dryness and calcining the residual ferrous sulphate to produce SO_2 and SO_3 ; separating SO_3 from SO_2 by combining the SO_3 with water and collecting it as sulphuric acid; introducing air and said SO_2 into the remaining portion of the liquor to convert SO_2 to a sulphate radical, the SO_2 and air being introduced in amounts sufficient to produce sulphuric acid in the liquor; and also adding to said liquor the sulphuric acid from the step of combining SO_3 with water, to produce a regenerated pickling liquor.

5. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include treating the spent liquor to divide ferrous sulphate contained therein into two portions of which one portion is in solid form and the other is in aqueous solution; introducing air and SO_2 into the aqueous solution of ferrous sulphate to promote conversion of SO_2 to a sulphate radical, the SO_2 and air being introduced in amounts sufficient to produce sulphuric acid and ferric sulphate in said solution; bringing the resulting solution into contact with SO_2 concentrated on an adsorbent, to reduce ferric sulphate to ferrous sulphate and to form sulphuric acid which raises the acid content of the solution; calcining the solid ferrous sulphate to produce SO_2 ; and utilizing the SO_2 so produced in the said conversion and reducing steps.

6. In a process of treating spent pickling liquor to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include introducing air and SO_2 into an aqueous solution containing ferrous sulphate obtained from spent pickling liquor to promote conversion of SO_2 to a sulphate radical, the SO_2 and air being introduced in amounts sufficient to produce sulphuric acid and ferric sulphate in said solution; and bringing the resulting solution into contact with SO_2 concentrated on an adsorbent to reduce ferric sulphate to ferrous sulphate and to form sulphuric acid which raises the acid content of the solution.

7. In a process of treating spent pickling liquor containing ferrous sulphate, the steps as in claim 6 in which a gas containing SO_2 is first intro-

duced in excess into the reduction step and the excess is subsequently introduced into the aqueous solution in the conversion step.

8. In a process of treating spent pickling liquor containing ferrous sulphate, the steps as in claim 6 in which SO_2 is dissolved in the solution during the reducing step to form sulphurous acid, and which includes the additional step of contacting the resulting solution with air to remove dissolved SO_2 .

9. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include treating the spent liquor to obtain solid ferrous sulphate; calcining said ferrous sulphate to produce SO_2 and SO_3 ; separating out the SO_3 by combining with water to form sulphuric acid; introducing air and said SO_2 into an aqueous solution of a metal salt which acts in the presence of air to promote conversion of SO_2 to a sulphate radical, said SO_2 and air being introduced in amounts sufficient to produce sulphuric acid in said solution; and adding to said solution sulphuric acid from the step of combining SO_3 with water, to aid in producing a regenerated pickling liquor.

10. In a process of treating spent pickling liquor containing ferrous sulphate and sulphuric acid to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include heating the spent liquor to remove water and produce a product containing solid ferrous sulphate and sulphuric acid; calcining said product to produce SO_2 and SO_3 ; separating out the SO_3 by combining with water to form sulphuric acid; and introducing air and said SO_2 into an aqueous solution of a metal salt which

acts in the presence of air to promote conversion of SO_2 to a sulphate radical to form sulphate radical in said solution.

11. In a process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid, the steps that include treating the spent liquor to obtain solid ferrous sulphate; calcining said ferrous sulphate to produce SO_2 and SO_3 ; separating out the SO_3 by combining with water to form sulphuric acid; and introducing air and said SO_2 into an aqueous solution of a manganese salt which acts in the presence of air to promote conversion of SO_2 to a sulphate radical, said SO_2 and air being introduced in amounts sufficient to produce sulphuric acid in said solution, to aid in producing a regenerated pickling liquor.

12. A process of treating spent pickling liquor containing ferrous sulphate to produce a regenerated liquor containing at least 15% sulphuric acid comprising the steps of introducing air into an aqueous solution containing ferrous sulphate obtained from spent pickling liquor, said air being introduced into the bottom portion of the solution in a relatively finely divided form so as to produce a mixture containing minute air bubbles dispersed throughout the solution; and separately and simultaneously introducing a gas containing SO_2 into said mixture, said gas being introduced at a point above that at which the air is introduced, the ferrous sulphate acting to promote conversion of SO_2 to the sulphate radical and the air and gas being introduced in the proper proportions to obtain an excess of air in the mixture so as to form sulphuric acid.

HARMON E. KEYES.

CERTIFICATE OF CORRECTION.

Patent No. 2,304,178.

December 8, 1942.

HARMON E. KEYES.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, lines 44 and 45, for "compression by the liquid. Nearer the surface by hydrostatic pressure of" read --compression by hydrostatic pressure of the liquid. Nearer the surface of--; page 6, first column, line 62, for " SO_4 " read -- SO_2 --; page 7, first column, line 38, for "possibly" read --possible--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of February, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

Patent No. 2,304,178 -

Granted December 8, 1942

HARMON E. KEYES

The above entitled patent was extended October 2, 1951, under the provisions of the Act of June 30, 1950, for 4 years and 81 days from the expiration of the original term thereof.

Commissioner of Patents.