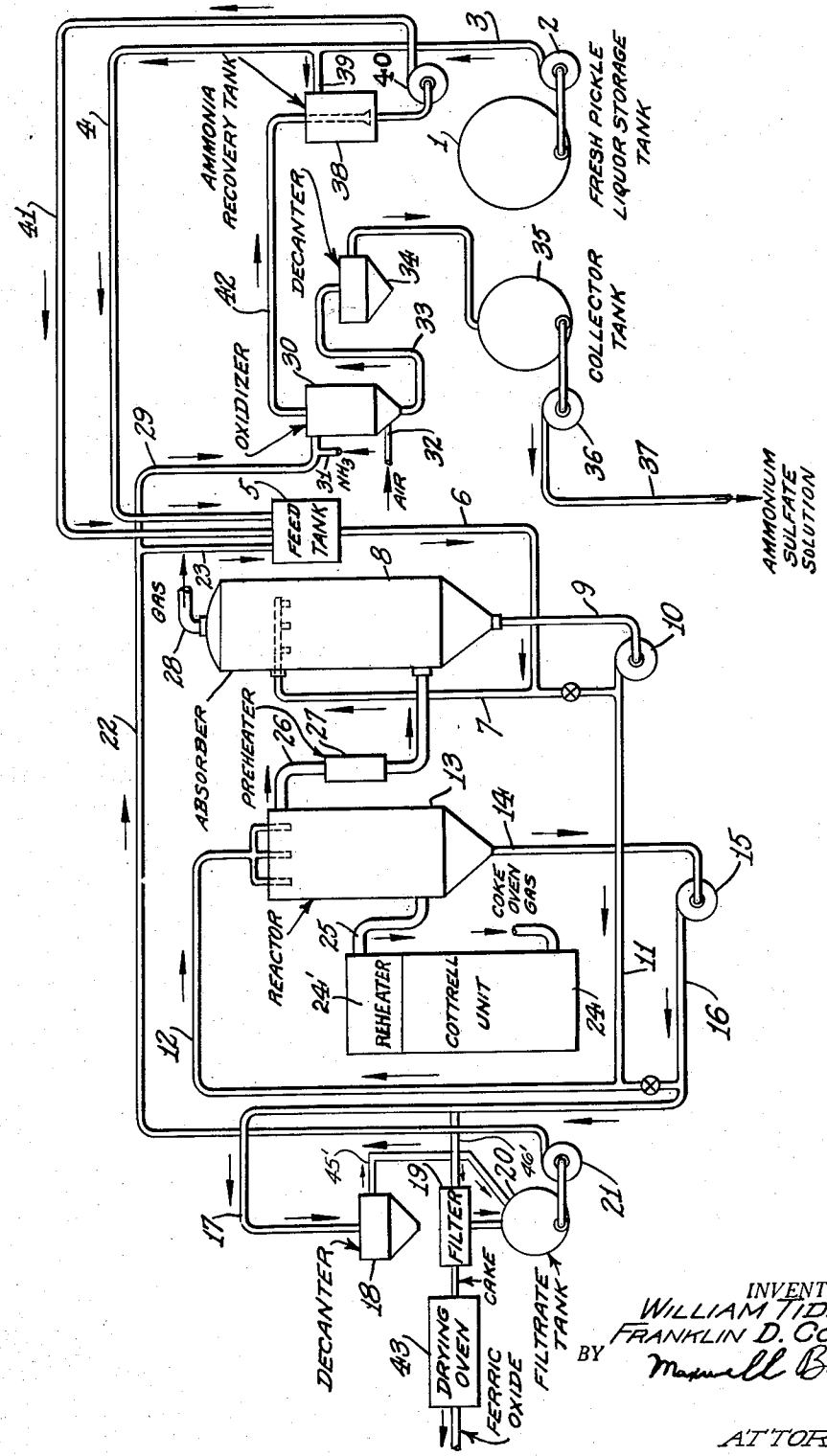
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METHOD FOR THE UTILIZATION OF IMPURE COKE OVEN GAS AND WASTE PICKLE LIQUOR IN THE MANUFACTURE OF AMMONIUM SULFATE

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METHOD FOR THE UTILIZATION OF IMPURE COKE-OVEN GAS AND WASTE PICKLE LIQUOR IN THE MANUFACTURE OF AMMONIUM SULFATE

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1

This invention relates to the utilization of coke oven gas and waste pickle liquor for the production of ammonium sulfate and more particularly to the production of ammonium sulfate, the removal of ammonia and other constituents from coke oven gas and the recovery of iron values from pickle liquor. Copending application Serial Number 672,895, filed May 28, 1946, relates to a similar process.

In the manufacture and processing of steel, a serious waste problem exists in disposing of the pickle liquor produced in the cleaning of steel with sulfuric acid. The annual production of waste pickle liquor amounts to about 800,000,000 gallons. Even if it cannot be utilized in the production of useful products, the pickle liquor, containing as it does free sulfuric acid, presents a serious problem of disposal. In fact, many communities prohibit the disposal of this liquor in streams or rivers unless it has been previously neutralized. At the present time a great portion of the pickle liquor is normally neutralized with lime before it flows into streams or rivers.

Frequently, steel manufacturing plants are located in close proximity to coke ovens. The coke oven gas contains ammonia, and processes have been suggested for utilizing the ammonia in the coke oven gas for neutralizing the ferrous sulfate and residual sulfuric acid in the pickle liquor. Since coke oven gas contains in addition other impurities such as cyanides and sulfides which also react with the ferrous sulfate in pickle liquor, one such proposed method involves initially separating the ammonia from the other constituents of the coke oven gas and then reacting the resulting ammonia with the pickle liquor. This procedure, however, involves operating difficulties which render it impractical for commercial practice and further involves an additional relatively expensive step. Many similar processes for the utilization of pickle liquor and coke oven gas which have been proposed are not economically feasible, and many steel manufacturers dispose of the pickle liquor without utilizing it for conversion into useful products.

In accordance with this invention, a cyclic process is provided which is economical in operation and which removes both the sulfate and iron values from the pickle liquor and ammonia and other constituents from unpurified coke oven gas. The utilization of the unpurified coke oven gas and the removal of ammonia from it is especially advantageous to steel manufacturers which are not infrequently adjacent the coke ovens which recover ammonia in the coke oven gas with purchased sulfuric acid. For such situations, in addition to utilizing both the pickle liquor and the ammonia in the coke gas for the production of a useful product, this process reduces the hazards of pickle liquor waste disposal.

2

An object of this invention is to remove substantially completely or materially reduce the ammonia contained in unpurified coke oven gas.

Another object of this invention is to utilize unpurified coke oven gas for the recovery of iron values from waste pickling solution and simultaneously to remove ammonia and other constituents from coke oven gas.

Another object of this invention is to provide an economic cyclic process for the production of ammonium sulfate by the utilization of unpurified coke oven gas and pickling liquor whereby the ammonia is removed substantially completely from the coke oven gas and iron values are recovered from the pickling liquor.

Another object of this invention is to increase markedly the ease of removal of the precipitated iron compounds produced by the reaction of waste pickle liquor and coke oven gas.

In the process of this invention, unpurified coke oven gas is contacted intimately with a feed liquor comprising pickle liquor containing free sulfuric acid and ferrous sulfate and a liquor containing ammonium sulfate. The unpurified coke oven gas contains ammonia, cyanide and hydrogen sulfide and is ordinarily utilized without any prior removal of the ammonia, cyanide or hydrogen sulfide, although some partial removal of one or all of these constituents may have been made prior to contact with the feed liquor. In the contact between the unpurified coke oven gas and the feed liquor, soluble ammonium sulfate and insoluble ferrous hydroxide, ferrous sulfide and ammonium ferroferrocyanide are formed. The insoluble ferrous hydroxide, ferrous sulfide and ammonium ferroferrocyanide are separated from the liquor by any suitable means, such as filtration, decantation or centrifugation. After separation of the insoluble materials, a portion of the liquor is recycled with additional pickle liquor to contact the unpurified coke oven gas. Desirably, from 60 to 90%, and preferably from 70 to 80%, of the liquor is recycled to form the feed liquor in the process. The remaining portion of the separated liquor is oxidized by aeration, for example, to remove any residual ferrous sulfate in that portion of the clear liquor. The free ammonia content of this portion of the liquor should be in excess of that necessary to react with the sulfate radicals present to form ammonium sul-

fate. For this purpose, the ammonia content of this portion of the liquor is adjusted, if necessary, by addition of ammonia to the liquor prior to oxidation; thus the free ammonia content of the liquor should be at least 0.5 gram per liter, and when the ferrous sulfate content of the liquor is 2 to 4 grams per liter, the free ammonia content of the liquor should be about 0.8 gram per liter or higher. The resulting iron hydrate formed in the oxidation step is removed by any suitable means, such as decantation, filtration or centrifugation, and the ammonium sulfate, after such separation, is recovered from the clear liquor by any conventional means.

The ferrous sulfate content of the feed liquor after contact with the coke oven gas may fluctuate from 0 to 10 grams per liter; the contact of the coke oven gas with the feed liquor is regulated so that the liquor after contact contains not more than 10 grams of ferrous sulfate per liter and is preferably regulated so that the ferrous sulfate content of the liquor after contact with the gas is ordinarily within the range of 2 to 4 grams per liter. A concentration of at least 2 grams per liter of ferrous sulfate insures substantially that the insoluble ammonium ferroferrocyanide formed is not converted to soluble ammonium ferrocyanide. When the ferrous sulfate content of the liquor after contact with the gas is substantially 0 gram per liter, the free ammonia content of the liquor should not exceed 1.5 grams per liter in order to avoid formation of soluble ammonium ferrocyanide. The amount of ammonium sulfate in the feed liquor prior to contact with the gas is at least 100 grams per liter and is preferably at least 200 grams per liter. The ammonium sulfate content of the liquor increases during contact with the gas, the increase ordinarily being 35 to 40 grams per liter. Within limits, the concentration of the ammonium sulfate in the solution after contact with the unpurified coke oven gas may be controlled by regulating the proportion of recycled liquor to the pickle liquor forming the feed liquor. With a pickle liquor of known concentration of ferrous sulfate and sulfuric acid, this proportion can readily be determined.

The practice of the cyclic process of this invention involves material economic and engineering advantages. The recycling of ammonium sulfate solution provides a flexible means of controlling the volume of feed liquor relative to the gas, the dilution of the ferrous sulfate and sulfuric acid to be reacted with the unpurified coke oven gas and the concentration of the ammonium sulfate in the feed liquor. The addition of large quantities of ammonium sulfate solutions to pickle liquor promotes more efficient contact between the liquor and gas, whereby greater reactivity is achieved with the unpurified coke oven gas, by virtue of the increased volume of liquor affording more intimate contact with the gas as well as a greater dispersion of precipitate in the liquor, thereby minimizing entrapment of unreacted ferrous sulfate and sulfuric acid in agglomerates of precipitate. Further, the dilution of the liquor with respect to iron precipitated and the concentration of the ammonium sulfate is controlled by means of recycling liquor separated from the precipitate so that the absorption and reactor units operate without plugging and with minimum back pressure, producing a concentrated ammonium sulfate solution which can be economically evaporated for the production of ammonium sulfate. Another advantage of the dilution of the pickle liquor with ammonium sulfate solution is that a smaller quantity of precipitate is formed per unit volume of liquor treated whereby separation of such precipitate is facilitated. And, as will be described in detail later, the resulting precipitate may be separated by filtration markedly more effectively than the precipitate formed when pickle liquor is treated with purified coke oven gas. In addition, only a portion of the total iron in the pickle liquor is oxidized. In fact, it has been found in the practice of one specific embodiment of this invention that about 8 to 10% of the ferrous sulfate content of the original pickle liquor was oxidized, the other 90 to 92% having been removed as a result of contact with the unpurified coke oven gas.

Desirably in the practice of this invention, the unpurified coke oven gas is contacted with the feed liquor in a plurality of chambers, such as by passing the coke oven gas through two chambers in sequence and contacting the coke oven gas passing through these chambers countercurrently with the feed liquor. If two chambers are employed, the coke oven gas flows from a first chamber to a second chamber, while the feed liquor flows in countercurrent direction from the second chamber to the first chamber. In the second chamber in which the feed liquor is first introduced, the ammonia in the coke oven gas reacts primarily with the free sulfuric acid to remove the ammonia substantially completely. The feed to the second chamber is desirably adjusted so that complete removal of the ammonia from the coke oven gas is effected. In the first chamber in which the feed liquor is directed after passage through the second chamber and in which the coke oven gas is first introduced, the reactions which take place are primarily among the ammonia, hydrogen sulfide and cyanides of the coke oven gas and the iron sulfate contained in the feed liquor. Desirably the liquor after contact in the second chamber contains from 0 to 10 and preferably from 2 to 4 grams of ferrous sulfate per liter. The precipitated iron compounds in the feed liquor, after passage through the first chamber, may be removed by any suitable means such as decantation, filtration or centrifugation. After the liquor has been separated from the solid material, from 60 to 90% of the liquor, for example about 80%, is recycled with raw pickle liquor, which is introduced into the second chamber to provide continuous operation. The remainder of the separated liquor, for example about 20%, is contacted with air or oxygen to oxidize the ferrous sulfate dissolved in this portion of the liquor. Prior to contact with the air or oxygen, sufficient ammonia is introduced into the liquor to convert substantially completely the ferric sulfate produced in the oxidation step to ferric hydrate. A minimum of 0.5 gram per liter of ammonia has been found satisfactory for this purpose when the ferrous sulfate content of the liquor is 2–3 grams per liter. Any unused ammonia in this oxidation step is absorbed by fresh pickle liquor; and the liquor, after reacting with the unused ammonia, may be used as a component of the feed liquor introduced into the second chamber for contact with the coke oven gas. The ferric hydrate precipitated in the oxidation step is separated from the liquor and the ammonium sulfate recovered in the usual manner from the resulting liquor. Conventional concentrators or evaporators may be used for this purpose.

A more comprehensive understanding of this invention is obtained by reference to the accompanying drawing.

In the drawing, pickle liquor (which ordinarily contains from 2 to 8% of free sulfuric acid and from 10 to 22% of ferrous sulfate, but which may contain more or less of these components) is collected in a suitable tank 1 and is pumped through pump 2 from the tank 1 through conduits or pipes 3 and 4 to a feed tank 5. As described in detail later, the pickle liquor is intermixed in the feed tank 5 with partially neutralized pickle liquor from an ammonia recovery tank 38 and recycled liquor obtained after contact with unpurified coke oven gas. From the feed tank 5 the feed liquor which comprises the recycled liquor, the fresh pickle liquor and the partially neutralized pickle liquor flows through conduits 6 and 7 to an absorber 8. From the absorber 8 the feed liquor is pumped through a conduit 9 by a pump 10 through conduits 11 and 12 to a reactor 13. The absorber and reactor may be any suitable equipment for effecting intimate contact between the coke oven gas and feed liquor. Thus, for example, these elements may be substantially empty shells equipped at the top with a distributor for liquor and at the base with a distributor for the gas, or either or both may be towers packed with any suitable packing, e. g. refractory tile. From the reactor 13 the feed liquor is pumped through a conduit 14 by a pump 15 through conduits 16 and 17 to a decanter 18 which operates in a conventional manner to separate supernatant liquor from precipitated material. The clarified liquor flows through conduit 45' into filtrate tank 20. If desired, a filter 19 into which liquor from conduit 46' enters, may also be provided for effecting a more complete separation of the liquor from the precipitated material. The clear liquor is stored in a filtrate tank 20. From the filtrate tank the clear liquor is pumped by a pump 21 through a conduit 22. A portion, for example about 80%, of the total volume of the liquor passing through the conduit 22, is recycled through the absorber and reactor through a conduit 23, the outlet of the conduit 23 being directed into the feed tank 5. The remaining portion, for example about 20%, of the total volume of the liquor passing through the conduit 22 is passed through a conduit 29 to an oxidizer 30.

Unpurified coke oven gas is passed in countercurrent relation with the flow of the feed liquor through the reactor 13 and the absorber 8. Preferably, the unpurified coke oven gas is processed initially by passage through a Cottrell or tar removal unit 24. The unpurified coke oven gas flows from the Cottrell unit 24 through a conduit 25 to the reactor 13. The outlet of the conduit 25 in the reactor 13 is located desirably near the bottom thereof to ensure the countercurrent relationship between the coke oven gas and the feed liquor. The coke oven gas flows upwardly through the reactor through a conduit 26 to the absorber 8. The conduit 26 may be provided with a preheater 27 to raise the temperature of the gas prior to introduction into the absorber. In the absorber the residual ammonia in the coke oven gas is reacted with the feed liquor which flows countercurrently to the coke oven gas. The coke oven gas with substantially all of the ammonia removed therefrom passes through an outlet 28 in the absorber 8. The feed liquor is repeatedly recycled by pump 10 through the absorber 8 and conduits 7 and 9 and by pump 15 through reactor 13 and conduits 12 and 14 to maintain the necessary rates of flow of liquor through the reactor and absorber to effect the desired intimate contact between the gas and liquor. Liquor is fed from the absorber through conduit 11 to the recycling system for the reactor and from the reactor through conduit 17 to decanter 18 at substantially the rate at which liquor is fed through conduit 6 to the absorber.

As heretofore described, a portion of the liquor from the conduit 22, for example about 20% of the total volume of liquor passing through the conduit 22, is directed through a conduit 29 to an oxidizer 30. Prior to the introduction of the liquor into the oxidizer 30, the ammonia content thereof is raised to preferably within the range of from .7 to 1.5 grams per liter of free ammonia. This ammonia may be introduced into the liquor through a pipe 31. The ammonia for this purpose is substantially free from cyanides and may be obtained from any suitable source such as a fixed ammonia still. The liquor in the tank 30 is oxidized by means of air provided through a pipe 32. The solution in the oxidizer is blown with sufficient air, either continuously or intermittently, to remove substantially completely any ferrous sulfate remaining in the liquor and to convert the iron values contained therein to insoluble ferric hydrate. After treatment in the oxidizer, the liquor containing the precipitated ferric hydrate is passed through a conduit 33 to a decanter 34 or filter to remove the ferric hydrate therefrom. The decanted liquor is then collected in a suitable collecting tank 35, from which it may be removed by means of a pump 36 to a conduit 37 connected to any suitable apparatus for the recovery of ammonium sulfate in crystalline form.

To remove the small amount of ammonia evolved from the oxidizer, the air after passage through the oxidizer is brought in contact through a conduit or pipe 42 with pickle liquor in an ammonia recovery vessel 38, the pickle liquor being supplied to the vessel 38 from the conduit 3 through a conduit 39. After the pickle liquor has contacted the air containing the ammonia in the ammonia recovery tank 38, it is pumped by means of a pump 40 through a conduit 41 to the feed tank 5.

The precipitated product obtained from the filter 19 or the decanter 18 and which contains primarily iron hydrate and iron sulfide may, if desired, be converted substantially completely to iron oxide. From the decanter or filter the precipitate may be pumped to a continuous vacuum filter in which it is washed free from ammonium sulfate and subsequently delivered to a drier or heat treating oven 43. In the oven the filter cake may be heated in the presence of air. The resulting precipitate contains from 45 to 69% of iron depending upon the amount of iron hydroxide or iron oxide present. The presence of iron sulfide in the precipitate materially assists in reducing the heat required to dry or heat treat the precipitate.

The advantage of utilizing unpurified coke oven gas, containing as it does hydrogen sulfide and resulting in the inclusion of iron sulfide in the precipitate, was demonstrated by a comparison of the filtration rates of the precipitate obtained from the neutralization of pickle liquor in the apparatus shown in the drawing with purified and unpurified coke oven gas. The purified coke oven gas was substantially freed of cyanides and sulfides, but contained ammonia prior to

introduction through conduit 25 to the reactor 13. The feed liquor introduced into the absorber 8 through the conduit 7 had the identical composition whether neutralized with the purified or unpurified coke oven gas and contained 51 grams per liter of ferrous sulfate and 2 grams per liter of sulfuric acid. When purified gas was employed for the neutralization of the feed liquor, the rate of filtration of the precipitate contained in the liquor passing from the reactor 13 through the conduit 14 was 7.2 pounds of dry filtration cake per hour, per square foot of filter surface, whereas when unpurified coke oven gas was used, the filtration rate under the same conditions was 48 pounds of dry cake per hour per square foot of filter surface. With the purified coke oven gas, the filter cake was ⅛ inch in thickness, and the composition of the cake substantially all ferrous hydrate; while with the unpurified coke oven gas the thickness of the cake was ¾" and the composition about 80% ferrous sulfide and the remainder ferrous hydrate and some insoluble ammonium ferroferrocyanide. Accordingly, a substantial increase in efficiency in the removal of the precipitate was achieved by utilizing unpurified instead of purified coke oven gas. When unpurified coke oven gas is used in accordance with this invention in the apparatus shown in the drawing, the composition of the wet filter cake from a 100% ammonia removal or a 90% ammonia removal from the coke oven gas is a mixture primarily of iron sulfide, iron hydrate and insoluble ammonium ferroferrocyanide. The iron sulfide content of the filter cake (dry basis) may vary from 35 to 95% and preferably should be between 75 and 95%, depending upon the proportions of hydrogen sulfide, ammonia and cyanides in the gas treated.

In the practice of the process of this invention in the apparatus illustrated in the drawing, the unpurified coke oven gas leaving the conventional Cottrell precipitator and reheater apparatus 24 and 24' flows upwardly through the reactor 13 and absorber 8 and then to suitable recovery apparatus through the conduit 26. Reheater 24' may be utilized to reheat the gas to temperatures conventionally employed in recovery of ammonia from coke oven gas. If desired, the gas may be heated between the reactor and absorber by preheater 27, for example, to avoid naphthalene deposits in the equipment. Addition of heat to the system may be accomplished by heating the feed liquor solution before entering the absorber to a temperature such that the temperature of the coke oven gas leaving the absorber 8 is maintained at or above the temperature of the gas entering the reactor 13, instead of by adding heat to the gas by means of reheaters 24' and 27.

The feed liquor leaving the tank 5 through the conduit 6 is a blend of pickle liquor supplied through conduit 4, partially neutralized pickle liquor supplied through conduit 41 and recycled liquor supplied through conduit 23. This mixture of recycled liquor and pickle liquor, which may contain a maximum of 100 grams per liter of ferrous sulfate and 50 grams per liter of sulfuric acid, and preferably contains at least 20 grams of ferrous sulfate and at least .2 gram of sulfuric acid per liter, passes first through the absorber 8 and then through the reactor 13. The composition of the feed liquor is so controlled that the amount of sulfate radicals in the feed liquor is approximately equivalent to the desired amount of sulfate radicals in the recycled liquor and the feed liquor is ordinarily so controlled that it contains sulfate radicals equivalent to more than 100, preferably more than 200, grams of ammonium sulfate per liter of recycled liquor. The flow of the feed liquor through the absorber and reactor is countercurrent to that of the coke oven gas passing through these chambers. The primary function of the absorber 8 is to remove substantially all of the ammonia from the coke oven gas leaving the reactor 13. The reaction in the absorber 8 is primarily the neutralization with ammonia of the free sulfuric acid in the feed liquor supplied through the conduit 7. In the absorber 8, the sulfuric acid is preferably substantially completely neutralized. In the drawing, the reactor 13 and the absorber 8 are two distinct pieces of apparatus. It is possible to design the equipment to incorporate the two units in one, but it has been found that better control is obtained when the reactor is separated from the absorber. Desirably, the rate of flow of feed liquor to the absorber 8 is adjusted so that substantially complete removal of ammonia from the coke oven gas is effected. If the removal of a lesser quantity of ammonia from the coke oven gas is desired, for example a 90% ammonia removal, the rate of flow of the feed liquor and coke oven gas to the reactor 13 and absorber 8 is regulated to effect this requirement. This regulation can be obtained by any suitable means such as valves (not shown) in the conduit 7 and 25. The free sulfuric acid content of the liquor leaving the absorber is ordinarily below .3 gram per liter of sulfuric acid although it may attain a maximum of 2 grams per liter or higher of free sulfuric acid.

After the feed liquor has passed through the absorber 8, it is contacted with the coke oven gas in the reactor 13. The primary function of the reactor 13 is to precipitate the greater amount of the ferrous sulfate from the feed liquor solution after it has left the absorber, and the contact time of the liquor with the gas is controlled so that the solution withdrawn from the reactor 13 through the conduit 14 has no soluble ammonium ferrocyanides and from 2 to 10 and preferably from 3 to 4 grams of ferrous sulfate per liter. One method of controlling the contact time of the gas and liquor in the reactor 13 is by regulating, for example by means of valves (not shown) in conduits 6 or 12, the amount of liquor and gas passing through the absorber 8 and reactor 13.

The principal reactions which take place in the reactor 13 are among the ammonia, hydrogen sulfide and cyanides in the gas and the ferrous sulfate in the feed liquor. The ferrous sulfate reacts with the sulfide and ammonia in the gas to produce respectively iron sulfide, ferrous hydroxide and ammonium sulfate. Some of the ferrous sulfate reacts with the cyanides in the gas to produce insoluble ammonium ferroferrocyanide. In the use of the apparatus shown in the drawing, it has been found that no soluble ammonium ferrocyanide is formed in operating under conditions such that the solution leaving the reactor 13 contains about 3 grams per liter of ferrous sulfate. Complete or substantial elimination of the ferrous sulfate from the pickle liquor in the reactor is desirably avoided since with reduced feed to the reactor 13 and substantially complete elimination of the ferrous sulfate from the pickle liquor, a considerable amount of soluble ammonium ferrocyanide may be formed when

the free ammonia content of the solution leaving the reactor 13 is in excess of 1.5 grams per liter.

The solution leaving the reactor at normal gas temperatures is pumped by means of a pump 15 to the decanter 18, and the solution may be filtered through the filter 19 to assure substantially complete removal of the precipitated iron compounds. The supernatant liquor from the filtration is stored in the filter tank 20 and is recycled and blended with raw pickle liquor in the feed tank 5 to produce a feed liquor of such concentrations that (1) the resulting feed liquor contains at least 100 grams of ammonium sulfate per liter and preferably at least 200 grams of ammonium sulfate per liter and (2) the volume and consistency of the precipitated iron hydrate and iron sulfide is controlled so that no blocking or high pressure differential exists in the absorber 8 or reactor 13.

The liquid withdrawn from the tank 20 which is not recycled and which ordinarily comprises a minor portion, for example about 20% of the liquor, is subjected to oxidation conditions to convert the remaining ferrous sulfate to insoluble iron hydrate by passage through the oxidizer 30. The ammonia content of the solution leaving the absorber 8 or the reactor 13 desirably varies from 0.1 to 1.0 gram per liter. If necessary, therefore, prior to passage through the oxidizer 30, the ammonium content of the supernatant liquid is increased to contain at least 0.5 gram per liter of free ammonia. The primary purpose of the oxidizer is to eliminate the remaining ferrous sulfate in the solution leaving the reactor 13 so that ammonium sulfate substantially free from iron can be obtained in the crystallization step. The reaction which takes places is among free ammonia, oxygen and ferrous sulfate at atmospheric temperatures. The ferrous sulfate is oxidized and the ammonia precipitates as ferric hydroxide, while the sulfate radical is converted to ammonium sulfate. Substantially complete removal of the ferrous sulfate is effected when the ammonia in the feed liquor contains or is strengthened to 0.8 gram per liter and the original solution fed to the oxidizer contains from 3 to 4 grams per liter of ferrous sulfate. The solution in the oxidizer is blown with air, after which substantially no ferrous sulfate exists in the solution and all of the iron has been converted to insoluble iron hydrate. The liquor containing the precipitated iron hydrate is transferred to a decanter 34 and the iron hydrate removed from the liquor. The clear liquor is then collected in a tank 35 from which the ammonium sulfate may be recovered by any well known means. If desired, a filter may be installed between the oxidizer 30 and the decanter 34 or between the decanter 34 and collector tank 35 to remove any suspended iron hydrate carried in the supernatant liquor.

To recover the small amount of unused ammonia from the oxidizer 30, the air released from the oxidizer is contacted with fresh pickle liquor in the ammonia recovery tank 38, and the free sulfuric acid in the pickle liquor readily absorbs this ammonia. The pickle liquor, after absorption of the ammonia, passes through conduit 41 to the feed tank 5.

The oxidation step may be omitted, if the presence of a small amount of iron in the ammonium sulfate recovered by the method is not objectionable. In that procedure, the separated liquor passing through the pipe 29 is directly processed to recover the ammonium sulfate from it by any conventional means, such as evaporation. However, substantially iron-free ammonium sulfate is ordinarily required, and the method desirably includes the oxidation step.

The rates of flow of the coke oven gas and pickle liquor, together with other data of two typical runs in the apparatus shown in the drawing are as follows:

	1st Run	2nd Run
Gas rate of coke oven gas, cu. ft. per hr.	10,000	10,000
NH_3 content of gas, Lb. per 10,000 cu. ft.	6	6
Pickle liquor used:		
Composition—		
$FeSO_4$, per cent	18.88	16.7
H_2SO_4, per cent	2.64	8.5
Volume per hour, Percent of feed to absorber or reactor (Remaining 78-80 percent is recycled liquor)	20-22	23.6
Feed to absorber:		
Composition—		
$FeSO_4$, G. p. l.	50.0	49.0
H_2SO_4, G. p. l.	7	25.0
Rate, Gallons per hour	52	36.8
Feed to reactor, Gal. per hour	52	36.8
Feed to thickener or decanter, Gal. per hour	52	36.8
Volume of filtrate plus clarified liquor from decanter or thickener plus water washing of cake, Gal. per hour	55	39.3
Volume returned to system for blending with fresh pickle liquor, Gal. per hour	41	28.1
Volume to oxidizer, Gal. per hour	14	11.2
Volume to collector tank for ammonium sulfate recovery unit, Gal. per hour	14	11.2
Composition, G. p. l. $(NH_4)_2SO_4$	220	300
Filter cake produced from filtration of thickened slurry from decanter, Pounds	48.1	33.2
Composition of wet washed cake (dry basis):		
FeS, percent	89	89
Insoluble ammonium ferroferrocyanide, percent	7	7
Iron hydrate, percent	4	4
Moisture content of filter cake, percent	65	65
Weight of cake dried at 105° C., Pounds	13.7	9.5
Ammonia recovery, percent (approx.)	100	100

It will be obvious from the above description that various changes may be made without departing from the scope of the invention. Thus, for example, while for the purpose of economy we prefer to blend recycled liquor containing ammonium sulfate with the pickle liquor to form the feed liquor employed in the process, the pickle liquor may be blended with ammonium sulfate solution from other sources to form the feed liquor. Further, the liquor from the reactor (after separation of precipitate) may be continuously introduced both into the feed tank and oxidizer, or may be alternately fed to the tank and oxidizer for time periods such that the desired proportions of the liquor are recycled and oxidized. Blending of the pickle liquor and recycled liquor may be accomplished in the presence of the coke oven gas, for example, by separately spraying the liquors into the top of the absorber. Ammonia from any desired source, e. g. the conventional ammonia still, may be utilized at any point in the process, for example, such ammonia may be mixed with the coke oven gas before it enters the reactor or the absorber, or may be introduced into the feed tank to neutralize partially the pickle liquor before entry of the liquor into the absorber.

Further, it is unnecessary to pass the coke oven gas through the absorber in contact with pickle liquor. Thus, pickle liquor may be blended with recycled liquor to obtain feed liquor containing preferably not more than 25 grams of free sulfuric acid per liter and this feed liquor may be introduced directly into the reactor or the equivalent. In order to obtain feed liquor of desired low free sulfuric acid content for introduction directly into the reactor, it may be desirable to neutralize partially the pickle liquor before in-

troduction into the reactor with extraneous ammonia or scrap iron before or after blending the pickle liquor with the recycled ammonium sulfate solution. When the feed liquor is introduced directly into the reactor, it is desirable to remove residual ammonia from the gas leaving the reactor by reaction with a mineral acid, e. g. in a saturator or scrubber.

As hereinabove described, contact between the coke oven gas and the liquor is preferably effected in countercurrent manner in suitable towers. However, the gas may be intimately contacted with the liquor in other types of apparatus, for example, the gas may be passed through saturator-type chambers containing bodies of pickle liquor diluted with recycled liquor containing ammonium sulfate while maintaining the precipitate suspended in the liquor by agitation. Recycled liquor and pickle liquor may be added to the saturators as required and reacted liquor drawn off and filtered or decanted for oxidation and recycling to the chambers.

In carrying out the invention, it is important that the coke oven gas contain hydrogen sulfide and ammonia, but it is not essential that other constituents which are capable of being removed by conventional coke oven gas purification processes be present in the gas. Further, other inert gases containing ammonia and hydrogen sulfide may be utilized in accordance with the invention. The invention may be carried out at temperatures ordinarily employed in conventional processes for recovery of ammonia from coke oven gas, for example from 35° to 70° C.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A cyclic process for producing ammonium sulfate comprising contacting unpurified coke oven gas with a feed liquor comprising pickle liquor containing ferrous sulfate and free sulfuric acid and a recycled liquor containing ammonium sulfate, separating liquor from the resulting precipitate formed, recycling a portion of the separated liquor for blending with the pickle liquor to form said feed liquor for contact with the unpurified coke oven gas and oxidizing the remaining portion of the separated liquor.

2. A cyclic process for producing ammonium sulfate comprising contacting unpurified coke oven gas with a feed liquor comprising pickle liquor containing ferrous sulfate and free sulfuric acid and a recycled liquor containing ammonium sulfate, separating liquor from the resulting precipitate formed, recycling from 60 to 90% of the separated liquor for blending with pickle liquor to form said feed liquor for contact with the unpurified coke oven gas and oxidizing the remaining 40 to 10% of the separated liquor.

3. A cyclic process for producing ammonium sulfate comprising contacting unpurified coke oven gas with a feed liquor comprising pickle liquor containing ferrous sulfate and free sulfuric acid and a recycled liquor containing ammonium sulfate, regulating the contact of the gas with the feed liquor so that the liquor, after contact, contains not more than 10 grams per liter of ferrous sulfate, separating liquor from the resulting precipitate formed, recycling a portion of the resulting clear liquor for blending with pickle liquor to form said feed liquor for contact with unpurified coke oven gas, adjusting the ammonia content of the remaining portion of said clear liquor to at least 0.5 gram of free ammonia per liter and oxidizing said remaining portion.

4. A cyclic process for producing ammonium sulfate comprising passing unpurified coke oven gas through a plurality of chambers in sequence, passing through said chambers a feed liquor comprising pickle liquor and recycled liquor containing ammonium sulfate, in countercurrent relation to the coke oven gas whereby the ammonia in the coke oven gas initially reacts primarily with the iron salts in the feed liquor, and the residual ammonia in the coke oven gas after the initial reaction is removed substantially completely by reaction primarily with the sulfuric acid of the feed liquor, separating the liquor from the precipitated iron compounds formed, recycling a portion of the resulting clear liquor for blending with the pickle liquor to form said feed liquor and oxidizing the remaining portion of the resulting clear liquor.

5. A cyclic process for producing ammonium sulfate comprising passing unpurified coke oven gas through a first chamber and a second chamber in sequence, passing a feed liquor comprising a blend of pickle liquor and recycled liquor containing ammonium sulfate through said second chamber and said first chamber in sequence, in countercurrent relation to the flow of the coke oven gas for contact therewith, separating the liquor from the precipitated compounds formed in the feed liquor after passage through said chambers, recycling a sufficient portion of the separated liquor for blending with pickle liquor to form said feed liquor so that the feed liquor prior to contact with the coke oven gas contains at least 100 grams of ammonium sulfate per liter and oxidizing the remaining portion of said separated liquor to convert the residual ferrous salts to the ferric compounds.

6. A process for removing ammonia from unpurified coke oven gas and recovering iron values from waste pickle liquor comprising intimately contacting unpurified coke oven gas with pickle liquor, separating the liquor from the precipitated product formed, contacting a portion of the resulting separated liquor with unpurified coke oven gas, oxidizing the remaining portion of said separated liquor and separating the precipitated product therefrom.

7. In the process of removing ammonia from unpurified coke oven gas and recovering iron values from pickle liquor, the steps comprising substantially completely removing the sulfuric acid from the pickle liquor and reducing the ferrous sulfate content thereof to between 2 and 10 grams per liter, separating the precipitated iron compounds formed, adjusting the ammonia content of the resulting clear liquor to at least 0.50 gram per liter of ammonia and passing air through the liquor to precipitate substantially completely the residual iron salts in said liquor.

8. In the process of removing ammonia from unpurified coke oven gas and recovering iron values from waste pickle liquor, the steps comprising substantially completely removing the sulfuric acid from a pickle liquor and reducing the ferrous sulfate content thereof to between 2 and 10 grams per liter, separating the precipitated iron compounds formed, adjusting the ammonia

content of the resulting clear liquor to at least .50 gram per liter of ammonia, passing air through the liquor to precipitate substantially completely the residual iron salts in said liquor and recovering the excess ammonia in the air after passage through said liquor by contacting with pickle liquor.

9. In the process of removing ammonia from coke oven gas and recovering iron values from waste pickle liquor, the steps which comprise contacting countercurrently coke oven gas with waste pickle liquor at a rate sufficient to remove substantially completely the sulfuric acid content thereof and reduce the iron sulfate content to 2 to 10 grams per liter, separating the precipitated iron compounds, adjusting the ammonia content of the resulting clear liquor to greater than 0.5 gram per liter, and aerating the clear liquor.

10. A process for removing ammonia from coke oven gas and recovering iron values from pickle liquor comprising passing coke oven gas successively through a first and a second chamber, passing a feed liquor comprising a pickle liquor and a recycled liquor containing ammonium sulfate successively through said second chamber and said first chamber, contacting countercurrently in said first chamber and said second chamber the coke oven gas with the feed liquor passing therethrough, the rate of flow of the coke oven gas through said first chamber and said second chamber being regulated so that the ammonia in the coke oven gas is substantially completely removed after passage through said second chamber and the amount of ferrous sulfate in the feed liquor after passage through said first chamber contains not less than 2.0 grams per liter, separating the resulting precipitate from the feed liquor after passage through said first chamber, recycling a portion of the resulting clear feed liquor successively through said second chamber and said first chamber, increasing the ammonia content of the remaining portion of said clear feed liquor to contain at least .50 gram of ammonia per liter, oxidizing said remaining portion, separating the precipitated product, contacting any unused ammonia obtained from the oxidation step with pickle liquor and adding the resulting partially neutralized pickle liquor to the feed liquor for contact with coke oven gas in said second and said first chamber.

11. A process for the recovery of ammonia as ammonium sulfate from gases containing ammonia and hydogen sulfide, which compises intimately contacting the gas with pickle liquor containing free sulfuric acid and iron sulfate, whereby the major portion of the iron in the pickle liquor is precipitated and the ammonia in the gas reacts with the sulfate radicals of the liquor to form ammonium sulfate, withdrawing liquor from the zone of contact, separating withdrawn liquor containing dissolved ammonium sulfate and ferrous sulfate from the precipitate, and oxidizing separated liquor with air in the presence of free ammonia to form additional ammonium sulfate.

12. A cyclic process for recovering ammonia from unpurified coke oven gas containing ammonia, hydrogen sulfide and cyanogen compounds and recovery of iron values from pickle liquor containing free sulfuric acid and ferrous sulfate, which comprises blending pickle liquor containing free sulfuric acid and ferrous sulfate with recycled liquor containing ammonium sulfate to produce feed liquor containing from .2 to 50 grams of free sulfuric acid, from 20 to 100 grams of ferrous sulfate and at least 100 grams of ammonium sulfate per liter of the feed liquor, passing said unpurified coke oven gas through reactor and absorber chambers in sequence, passing said feed liquor first through the absorber and then through the reactor in countercurrent relation to the coke oven gas, whereby the ammonia, hydrogen sulfide and cyanogen compounds present in the coke oven gas initially react in the reactor chamber primarily with the iron salt in the feed liquor to form ammonium sulfate and to precipitate iron hydrate, iron sulfide and ammonium ferroferrocyanide and the residual ammonia present in the coke oven gas is removed substantially completely by reaction in the absorber chamber primarily with the sulfuric acid of the feed liquor, regulating the flow of feed liquor through said chambers so that the ferrous sulfate content of the liquor leaving said reactor chamber does not exceed 10 grams per liter and the free ammonia content of the liquor leaving the reactor chamber falls within the range of .1 to 1 gram per liter, separating the precipitate from the liquor leaving the reactor chamber, recycling from 60% to 90% of the separated liquor to the absorber chamber with pickle liquor for contact with additional coke oven gas, passing an oxygen-containing gas through the remainder of said separated liquor in the presence of at least .5 gram per liter of free ammonia, whereby substantially all of the sulfate radical in said oxidized liquor is reacted to form ammonium sulfate and the iron values in the liquor are converted to iron hydrate, and separating the iron hydrate from the resultant ammonium sulfate solution.

13. A process as defined in claim 12 in which the ferrous sulfate content of the liquor leaving the reactor chamber is substantially maintained within the range of from 2 to 4 grams per liter and the ammonium sulfate content of the liquor introduced into the absorber chamber is at least 200 grams per liter.

14. A process for recovery of ammonia as ammonium sulfate from gases containing ammonia and hydrogen sulfide and recovery of iron values from pickle liquor containing ferrous sulfate, which comprises forming a feed liquor containing at least 100 grams of ammonium sulfate, not more than 25 grams of free sulfuric acid, and from 20 to 100 grams of ferrous sulfate per liter, by blending ammonium sulfate solution with pickle liquor containing ferrous sulfate, intimately contacting said feed liquor with said gas, whereby iron values of said liquor are precipitated as iron hydrate and iron sulfide, separating the precipitate from the liquor, recycling a portion of the separated liquor together with pickle liquor into intimate contact with additional gas containing ammonia and hydrogen sulfide, and oxidizing the remainder of said liquor in the presence of free ammonia.

15. A cyclic process for recovery of ammonia as ammonium sulfate from gases containing ammonia and hydrogen sulfide, which comprises intimately contacting the gas with feed liquor comprising pickle liquor containing free sulfuric acid and iron sulfate and recycled liquor containing ammonium sulfate, whereby iron in the feed liquor is precipitated and ammonia in the gas reacts with sulfate radicals of the liquor to form ammonium sulfate, separating liquor containing dissolved ammonium sulfate from the precipitate, recycling a portion of the separated

liquor with additional pickle liquor into contact with additional coke oven gas and oxidizing the remaining portion of the separated liquor.

16. A process for removing ammonia from unpurified coke oven gas and recovering iron values from waste pickle liquor comprising intimately contacting unpurified coke oven gas with a ferrous sulfate liquor derived from pickle liquor, separating the said ferrous sulfate liquor from the precipitated product formed, contacting a portion of the resulting separated liquor with unpurified coke oven gas, oxidizing the remaining portion of said separated liquor and separating the precipitated product therefrom.

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