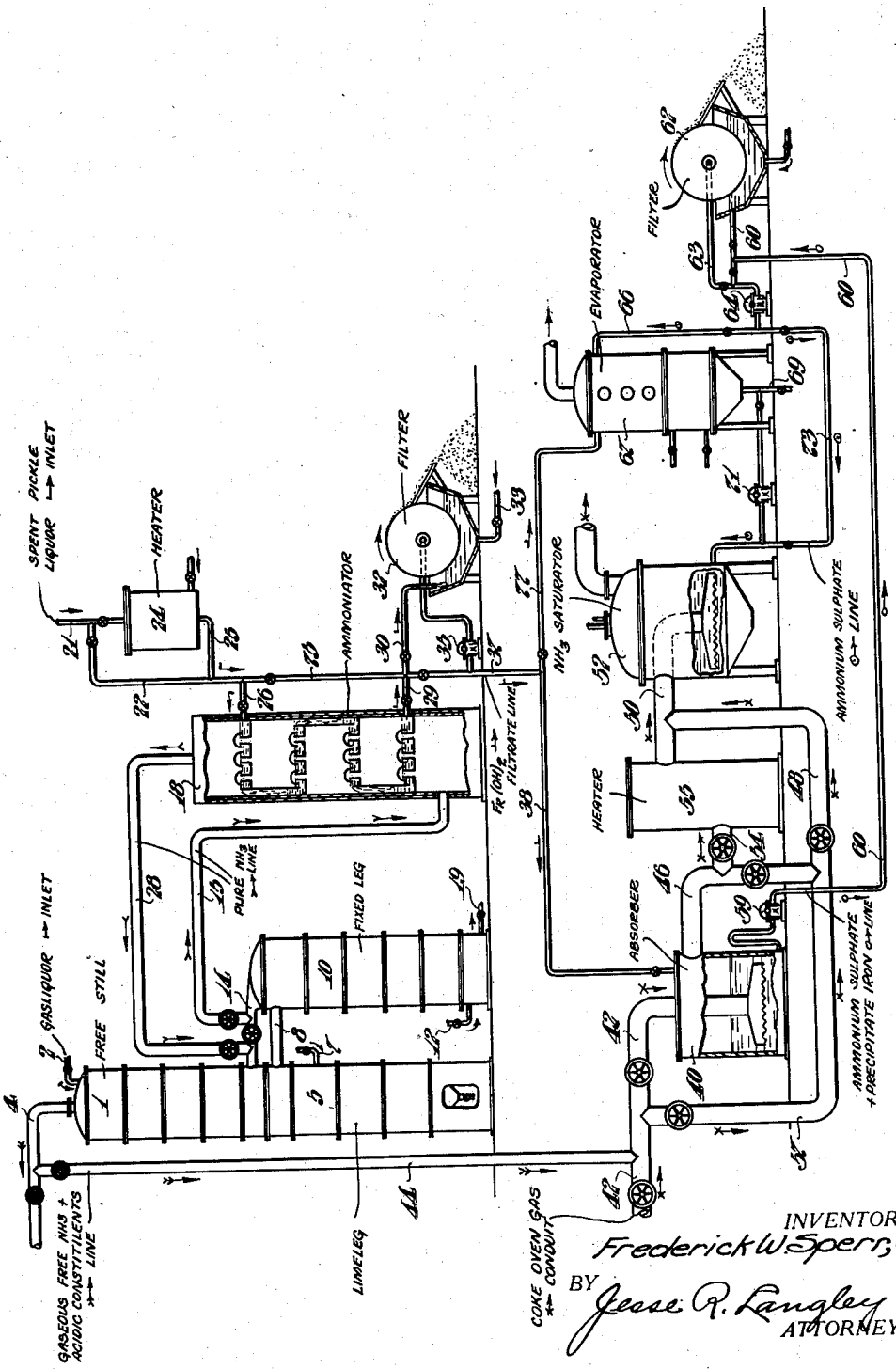
Jan. 8, 1935. F. W. SPERR, JR 1,986,900

PRODUCTION OF AMMONIA COMPOUNDS

Filed June 4, 1931



INVENTOR.
Frederick W. Sperr, Jr.
BY Jesse R. Langley
ATTORNEY.

Patented Jan. 8, 1935 1,986,900

UNITED STATES PATENT OFFICE

1,986,900

PRODUCTION OF AMMONIA COMPOUNDS

Frederick W. Sperr, Jr., Phoenix, Ariz., assignor to The Koppers Company of Delaware, a corporation of Delaware

Application June 4, 1931, Serial No. 541,992

13 Claims. (Cl. 23—119)

This invention relates to the production of useful compounds of iron and ammonia, and especially to the utilization of spent pickling liquor in the production of ammonium sulphate from ammonia contained in fuel gas.

It has been general practice in the preparation of iron and steel sheets, castings, and the like for galvanizing or tinning, and also in the cleaning of such objects, to pickle them in a bath of weak acid or to contact them with an acid solution in some other suitable manner. Sulphuric acid is the acid most frequently used in this pickling liquor, but hydrochloric acid and other acids are sometimes used. The acid dissolves the oxides of iron which are formed when hot iron and steel come in contact with air or moisture, and may also dissolve some of the metal itself, to form a solution of salts, such as ferrous and ferric sulphates or chlorides in which the ferrous salts usually predominate.

Fresh acid may then be added to the pickling liquor and it is then employed in the treatment of more ferrous objects. This procedure is repeated until the liquor becomes too dirty or too high in iron salts to be satisfactory for further use, and part or all of it is then replaced with a fresh acid solution. The replaced solution, known as waste or spent pickling liquor, must then be disposed of and this disposal has in the past been accomplished in several ways, as by neutralizing with iron and concentrating to recover iron salts, and by precipitating the iron with lime.

Typical spent pickling liquor discharged from a system in which H_2SO_4 has been used for acidification of the bath has a specific gravity of about 1.2 and contains ferrous sulphate usually amounting to about 25% or 30% and free sulphuric acid amounting to about 1%. It has previously been suggested that such pickling liquor or other solutions of iron salts be treated with raw coke oven gas or similar fuel gases or with ammoniacal liquor condensed therefrom to recover ammonia originally contained in the gas. The ammonia thus recovered is in the form of a salt such as ammonium sulphate, for example, and iron is supposed to be recovered chiefly in the form of a hydrate or hydroxide which may be sintered or otherwise treated in preparation for further use.

In such processes, and also in processes in which the pickling liquor is treated with a gas or vapor containing ammonia but substantially free from acidic constituents to precipitate iron, such as the process described in my copending application Serial No. 541,993, filed June 4, 1931, it was necessary in order to completely precipitate the iron to oxidize the liquor before or after ammoniation, as by aeration at atmospheric or higher pressures. This oxidation of the pickling liquor converted ferrous compounds present therein to the ferric state, and facilitated their removal, but was disadvantageous in other respects, since solutions of ferric compounds are quite corrosive to iron, steel and various other metals.

For that reason processes involving oxidation of the pickling liquor had to be carried out in special corrosion-resisting apparatus. Furthermore, oxidation of the liquor following ammoniation, by aeration, for example, does not by itself precipitate all the iron but must be followed by a second ammoniation if substantially complete removal of the iron is desired.

An object of my present invention is to provide an improved process of utilizing spent pickling liquor or other solutions of iron salts.

A second object of my invention is to provide an improved process of recovering ammonia from fuel gas.

Another object of my invention is to provide a process whereby ammonia obtained from fuel gas is economically recovered in the form of valuable salts, and suitable apparatus therefor.

A further object of my invention is to provide a process wherein spent pickling liquor and similar solutions are utilized in connection with the recovery of ammonia and other constituents from fuel gas to produce useful ammonium salts and iron compounds, and suitable apparatus therefor.

My invention has for further objects such other operative advantages and results as are found to obtain in the process and aparatus hereinafter described and claimed.

In my present invention the difficulties previously encountered in attempting to utilize spent pickling liquor and the like in the recovery of ammonia from fuel gases are overcome by first treating the pickling liquor with ammonia vapor from the fixed leg of an ammonia still of the type generally used in coke oven plants and elsewhere to recover ammonia from gas liquor and other liquids containing it in both free and fixed form. This ammoniation is followed by filtration and a further treatment of the iron salt solution with raw coke oven gas or other gas or vapor containing ammonia and H_2S, such as the vapor from a free ammonia still. Iron remaining in solution after the ammoniation is thereby precipitated in the form of ferrous sulphide and analogous compounds, and the necessity for oxidation is eliminated.

Fixed ammonia still vapors are normally quite free from H_2S, HCN, CO_2 and analogous impurities, and substantially complete freedom from such impurities can readily be insured if desired, as described in my copending application Serial No. 495,641, filed November 14, 1930, now Patent No. 1,928,510, issued Sept. 28, 1933. In my present process therefore the major portion of the iron content of the pickle liquor is precipitated as ferrous hydrate, $Fe(OH)_2$, substantially free from impurities. A similar result may be obtained by passing ammonia vapor from a free ammonia still through a desulphurizing stage, or otherwise freeing it from acidic impurities, and contacting pickle liquor or the like with this vapor, or by employing ammonia of suitable purity from some other source.

After removal of this precipitate, as by filtration, the pickle liquor is treated with raw coke oven gas or the like and acidic impurities in the gas, such as H_2S, complete the precipitation of the iron without oxidation. This second precipitate is then removed and a substantially pure solution of ammonium sulphate remains, from which the salt may be recovered in any suitable manner.

In the first stage of the process ammonia reacts with $FeSO_4$ and free H_2SO_4 in the pickle liquor to form ammonium sulphate and ferrous hydrate. The reaction

$$FeSO_4+2NH_3+2H_2O=Fe(OH)_2+(NH_4)_2SO_4$$

is reversible and consequently precipitation of iron is incomplete, but by overtreating with the ammonia vapor it is possible to precipitate 60% to 80% or more of the iron as ferrous hydrate. This precipitate is preferably filtered out while the liquor is still hot and the filtrate is then brought into contact with gas containing ammonia and H_2S and/or CO_2, with or without HCN.

In this stage a further quantity of ammonium sulphate is formed in the solution and the remaining iron is precipitated as ferrous sulphide, carbonate, ferrocyanide, or the like. If cyanogen compounds are present, it is desirable in this stage to so regulate the gas and liquor rates that there is always a trace of free $FeSO_4$ in the bath. If the iron is completely precipitated additional ammonia might react with ferrous ferrocyanide or other cyanogen compounds to form soluble ammonium ferrocyanide, which is undesirable since it may cause coloration of the final salt.

I now describe with reference to the accompanying drawing a preferred method of practicing my improved process of producing ammonium salts and useful iron compounds from spent pickling liquor or the like and constituents of fuel gas. In the drawing,

The single figure is a somewhat diagrammatic view, partly in elevation and partly in vertical section, of apparatus suitable for the practice of my invention.

Ammoniacal liquor, such as the gas liquor produced by cooling and partially condensing coke oven gas or other fuel gases, enters a free ammonia still 1 through a pipe 2. The liquor passes downwardly through this still in intimate contact with a countercurrent flow of steam or other hot vapor which removes free ammonia and other volatile constituents such as H_2S, CO_2 and the like from the liquor and carries them out of the still through a vapor outlet 4.

Liquor then continues downwardly from the free still into a lime mixing chamber or liming chamber 5 which may conveniently be located below the free still 1, and is there mixed with lime or other suitable alkaline material introduced through a pipe 7. This alkaline material converts fixed ammonia in the liquor to the free form and the liquor passes from the liming chamber 5 through a pipe 8 into a fixed ammonia still 10.

In this still 10 the liquor is subjected to further distillation with steam supplied through a pipe 12 which removes the ammonia remaining in the liquor, and vapor consisting essentially of ammonia and steam, and substantially free from acidic impurities, passes from the top of this still through pipes 14 and 15 into an absorber or ammoniator 18. Still waste substantially free from ammonia is discharged from the bottom of the fixed still 10 through a pipe 19 for disposal. Due to the back pressure of the absorber 18, it may be desirable to provide a pump for delivering liquor through pipe 8, or a blower for the vapor line 15.

Spent pickling liquor or an analogous solution of iron salts passes from pipes 21 and 22 or through pipe 21, a solution heater 24, and a pipe 25 into pipe 26 which delivers it to an upper section of the ammoniator 18. This ammoniator may be of any suitable type for providing intimate contact between the solution and the ammonia vapor, such as the bell-and-tray type shown in the present instance.

The spent pickle liquor passes downwardly through the ammoniator in intimate contact with the rising current of ammonia vapor and absorbs ammonia therefrom to form ammonium sulphate or the like in the solution and to precipitate iron, principally in the form of ferrous hydrate. The ammoniator is preferably well insulated to prevent radiation of heat and condensation of the vapor, and may also be heated if desired.

The remaining vapor, which may be substantially free from ammonia, passes from the top of the ammoniator through pipe 28 and is introduced into the bottom of the free still 1 where it is employed in the first distillation of a further quantity of gas liquor, if desired. Part of the vapor leaving the fixed still 10 may be allowed to pass directly through pipe 14 into the free still 1.

The ammoniated pickling liquor, which now consists of a suspension of $Fe(OH)_2$ in a solution containing ammonium sulphate and ferrous sulphate and usually some dissolved ferrous hydrate, is withdrawn from a lower section of the absorber 18 through pipes 29 and 30 to a filter 32, which is preferably of the continuous or vacuum type.

The solution in the reservoir of this filter may be agitated and/or heated if necessary, as by air or steam supplied through a pipe 33. The filter removes the suspended $Fe(OH)_2$ from the liquor, and the clear filtrate, together with any water used to wash the filter cake, is withdrawn by a pump 35 and delivered through pipes 37 and 38 to an absorber 40 which may be similar in construction to an ammonium sulphate saturator of the usual type, or to a wash box, or of other suitable form.

Coke oven gas or other fuel gas which is preferably substantially free from tar but contains ammonia and H_2S and/or CO_2 enters the absorber 40 through a pipe 42. In this pipe 42 the gas may be mixed with vapors from the free ammonia still, which pass from pipe 4 through a pipe 44 into the pipe 42, or the gas, or the vapor, or similar gases or vapors, may be admitted alone into the absorber 40.

In this absorber the gas or vapor is intimately

contacted with the pickle liquor, and the ammonia and H_2S react with the remaining ferrous sulphate to form ammonium sulphate and to precipitate ferrous sulphide (FeS). The gas then continues through pipes 46, 48, and 50 into a saturator 52 in which the ammonia remaining in the gas is removed.

As an alternative, the gas may pass from pipe 46 through pipe 54 into a reheater 55 in which its temperature is raised and then through pipe 50 into the saturator 52, or a reheater may be inserted in the line 42 before the absorber 40. Part or all of the gas may also be by-passed around the absorber 40 from pipe 42 to pipe 48 or 54 through a pipe 57.

The rates of flow of the gas entering the absorber 40 through pipe 42 and the iron salt solution supplied to the absorber through pipe 38 are preferably so adjusted that there is always a small amount of unconverted ferrous sulphate in the liquor, to prevent the formation of soluble ammonium ferrocyanide as described hereinabove.

Slurry consisting of a suspension of ferrous sulphide and/or other insoluble iron compounds in a solution containing ammonium sulphate and usually a small amount of ferrous sulphate is withdrawn from the absorber 40 by a pump 59 and delivered through a pipe 60 to a filter 62, which is preferably of the continuous type. In this filter the ferrous sulphide or other precipitates are removed, and a clear solution of ammonium sulphate is withdrawn from the filter through a pipe 63 by a pump 64.

This solution is delivered through a pipe 66 to an evaporator 67 in which the solution is concentrated. This concentration may be carried to such a point that ammonium sulphate crystallizes out of the mother liquor in the evaporator or after withdrawal therefrom through pipe 69, or the solution may be only partially concentrated before withdrawal from the evaporator 67, and then delivered by a pump 71 to the saturator 52 wherein it is further concentrated.

Alternatively, the evaporator 67 may be omitted, and the solution withdrawn from the filter by the pump 64 may be delivered directly through pipe 73 to the saturator 52, wherein all of the required concentration takes place. When part or all of the concentration of the solution is effected in the saturator, the gas entering the saturator must be sufficiently preheated to enable it to carry the desired amount of water, or strong acid must be supplied to the saturator bath. Ammonium sulphate produced from the pickling liquor is recovered from the saturator bath in the usual manner along with the sulphate ordinarily produced in the saturator.

As an alternative procedure, the first filtration in filter 32 may be omitted and the liquor withdrawn from the ammoniator 18 may pass directly from pipe 29 through pipes 37 and 38 into the absorber 40. In that case no pure iron hydrate is produced, and substantially all of the iron is recovered in the form of sulphide or analogous compounds.

Another alternative is to omit the first ammoniation, and the pickle liquor is then passed from pipe 22 through pipe 75 into pipe 37 and thence to the absorber 40, where the iron is entirely precipitated by constituents of the raw gas or ammonia vapor from the free still, as described.

In instances when a certain amount of iron in the final ammonium salt is not objectionable, as is sometimes the case when the salt is used for fertilizer, the second precipitation may be omitted and the solution after the first ammoniation or after the first filtration may be passed from pipe 37 through pipe 77 into the evaporator 67 where it is concentrated substantially to the crystallizing point and a fertilizing compound containing a variable amount of soluble and/or insoluble iron is recovered.

If soluble ferrocyanides, such as ammonium ferrocyanide, are not objectionable in the final product, it is not necessary to retain traces of ferrous sulphate in the solution in the absorber 40. The solution may then be overtreated with gas containing ammonia and H_2S or the like at this point to completely decompose the iron salt, and the ammonium salt is then recovered from the solution as before, but in this case it may contain ferrocyanides.

If HCN is removed from the gas before it enters the absorber 40, contamination of the product with ferrocyanide is prevented under any circumstances, as described in the copending application of Caleb Davies, Jr., Serial No. 535,637, filed May 7, 1931 now Patent No. 1,942,050, issued Jan. 2, 1934.

It will be obvious to those skilled in the art that various modifications can be made in the several parts of my apparatus and the several steps of my process other than those enumerated hereinabove, and it is my intention that the claims shall cover such modifications as are included within the scope thereof.

I claim as my invention:

1. The process of manufacturing ammonium salts which comprises contacting a solution of an iron salt first with ammonia vapor substantially free of acidic constituents thereby precipitating iron, removing said iron before the solution is further treated with an acidic constituent to form an insoluble compound with the iron thereof, and thereafter contacting the solution with a gas having a constituent which forms an insoluble compound with iron, thereby forming ammonium salt in the solution and precipitating iron, and recovering ammonium salt from the solution.

2. In a process of manufacturing ammonium salts the steps of contacting a solution of an iron salt first with ammonia vapor substantially free from acidic constituents, thereby forming ammonium salt in the solution and precipitating iron, removing said iron, thereafter contacting the solution with gas containing an acidic constituent which forms an insoluble compound with iron, and recovering ammonium salt from the solution.

3. The process of manufacturing ammonium salts which comprises contacting a pickle liquor solution of an iron salt first with ammonia vapor substantially free from acidic constituents from gas liquor to form ammonium salt in the solution and to precipitate iron hydrate, removing iron hydrate substantially free from insoluble impurities from the solution, thereafter contacting the solution with a gas containing one or more acidic compounds from the group including H_2S, HCN and CO_2 to precipitate a further quantity of iron, removing said iron, and recovering ammonium salt from the solution.

4. The process of manufacturing ammonium salts which comprises contacting a pickle liquor solution of an iron salt first with ammonia vapor substantially free from acidic constituents which forms an insoluble compound with iron to form ammonium salt in the solution and to precipitate

iron hydrate, removing iron hydrate from the solution, thereafter contacting the solution with a gas containing ammonia and an acidic constituent which forms an insoluble compound with the iron thereof to precipitate iron therefrom and to form a further quantity of ammonium salt in the solution, removing said iron, and recovering ammonium salt from the solution.

5. The process of manufacturing ammonium salts which comprises contacting a solution of an iron salt with ammonia vapor substantially free from acidic constituents to form ammonium salt in the solution and to precipitate iron hydrate, removing iron hydrate from the solution, contacting the solution with a gas containing ammonia and hydrogen sulphide to form a further quantity of ammonium salt and to precipitate iron sulphide, removing iron sulphide from the solution, and recovering ammonium salt from the solution.

6. The process of manufacturing ammonium salts from gas liquor and pickle liquor, which comprises distilling the gas liquor to remove volatile constituents therefrom in the form of a gas containing ammonia and acidic constituents of the gas liquor, separately removing fixed ammonia from the residue of the gas liquor in the form of ammonia vapor substantially free from acidic constituents, contacting this vapor with the pickle liquor comprising an iron salt solution to precipitate iron and to form ammonium salt in the solution before treatment of the pickle liquor with acidic constituents, removing precipitated iron compounds from the so treated pickle liquor solution, thereafter contacting the pickle liquor solution with said gas containing an acidic constituent which forms an insoluble compound with iron, removing the insoluble iron, and recovering ammonium salt from the solution.

7. The process of recovering ammonia in the form of ammonium salts from gas liquor and an iron salt solution, which comprises distilling said liquor to remove free ammonia together with other volatile acidic constituents, subjecting the liquor to further treatment for separately removing fixed ammonia in the form of vapor substantially free from acidic constituents, contacting the iron salt solution first with this vapor to precipitate iron hydrate and to form ammonium salt in the solution, removing iron hydrate from the solution, thereafter contacting the solution with gas having an acidic constituent which precipitates a further quantity of iron, and recovering ammonium salt from the solution.

8. The process of recovering ammonia from gas liquor, which comprises distilling said liquor in a free ammonia still to remove volatile constituents, treating the liquor with alkaline material to liberate fixed ammonia, transferring the treated liquor to a fixed ammonia still wherein it is subjected to a second distillation to obtain ammonia vapor substantially free from acidic constituents, contacting this vapor at an elevated temperature with a solution containing iron salt to precipitate iron and to form ammonium salt in the solution, removing the precipitated iron, thereafter contacting the resulting ammonium salt solution with gas from the aforesaid free ammonia distillation step containing ammonia and hydrogen sulphide, removing insoluble iron compounds from the solution, and recovering ammonium salt from the solution.

9. The process of manufacturing ammonium sulphate and iron compounds from gas liquor and pickle liquor comprising an iron sulphate solution which comprises removing free ammonia together with volatile acidic constituents from gas liquor, treating the residual liquor with alkaline material, distilling the treated liquor to obtain ammonia vapor substantially free from acidic impurities, first contacting the solution containing iron sulphate with vapor from the last mentioned distillation step to precipitate iron hydrate and to form ammonium sulphate in the solution, removing iron hydrate from the solution, and thereafter contacting the solution with gas from the aforesaid free ammonia distillation step containing ammonia and hydrogen sulphide, removing iron sulphide thereby formed, and recovering ammonium sulphate.

10. The process of manufacturing ammonium salts which comprises contacting a solution of iron salt first with a gaseous mixture containing steam and ammonia at such temperature that the steam is substantially uncondensed, thereby forming ammonium salt in the solution and precipitating iron, removing the precipitated iron, thereafter contacting the solution with a gas containing a compound which precipitates a further quantity or iron, removing said further quantity of iron and recovering ammonium salt from the solution.

11. The process of manufacturing ammonium salts, which comprises contacting iron pickling liquor with ammonia vapor substantially free from acidic impurities to precipitate iron hydrate and to form ammonium salt in solution, removing iron hydrate from the solution, contacting the solution with gas containing ammonia and hydrogen sulphide to form a further quantity of ammonium salt and to precipitate iron sulphide, removing iron sulphide from the solution, concentrating the solution, and recovering ammonium salt therefrom.

12. The process of manufacturing ammonium salts which comprises contacting an iron salt solution with ammonia vapor from a fixed ammonia still, removing iron hydrate thereby precipitated from the solution, contacting the solution with gas containing ammonia and an acidic constituent which forms an insoluble compound with iron, removing insoluble iron compound precipitated thereby, concentrating the solution, and recovering crystallized ammonium salt from the solution.

13. The process of recovering ammonia from fuel gas in the form of ammonium salt, which comprises treating a stream of said gas to remove free ammonia and substantially all of the fixed ammonia therefrom in the form of gas liquor, removing free ammonia together with other volatile acidic constituents from the gas liquor, separately removing fixed ammonia from the liquor in the form of ammonia vapor substantially free from acidic constituents, contacting this vapor with an iron salt solution to precipitate iron hydrate and to form ammonium salt in solution, separating iron hydrate from the ammoniated iron salt solution, thereafter contacting the solution with at least a portion of the gas resulting from the step of removing free ammonia together with acidic constituents from the gas liquor to substantially complete the precipitation of iron and to form a further quantity of ammonium salt, removing iron precipitate from the solution, and recovering ammonium salt from the solution.

FREDERICK W. SPERR, JR.