

TREATMENT OF CONTAMINATED STRETTFORD SOLUTIONS
IN GAS PURIFICATION

5 The present invention relates to recovering
the anthraquinone disulfonate and vanadate from
Stretford process solutions used in gas purification,
and the recycling of the anthraquinone disulfonate
and vanadate to the process solution.

10 The Stretford process is well known in the
art of gas purification for the removal of H_2S from
"foul gas" or "tail gas" streams of various compositions
and origins, such as gas streams resulting from refining
of petroleum or coal products. The Stretford process
15 employs, fundamentally, an alkaline aqueous solution
comprising a salt of an anthraquinone disulfonic acid,
such as Na_2 -ADA, and a vanadium salt, such as sodium
vanadate. During its use, the Stretford solution
acting on the H_2S and other gas components, builds up
20 various levels of side-products such as sodium
thiosulfate, sodium sulfate, and various alkalinities
such as sodium carbonate and sodium bicarbonate, due to
reaction with the alkali (preferably NaOH) employed to
maintain the solution alkaline

In one embodiment, the present invention is directed to a process whereby a portion of the Stretford solution is removed as a side-stream in order to maintain the build-up of various side-products to a controllable, allowable concentration, the process being particularly effective in substantially removing sodium sulfate and sodium thiosulfate in the side-stream, while recovering a substantial amount of the NaADA or Na₂ADA and the vanadium salt, both of these components being recycled to the Stretford solution. Thus, as the Stretford solution is continuously cycled through its use step and through its recovery, clean-up, and replenishment steps, the level of undesirable sulfate and thiosulfate is effectively controlled, the loss of expensive NaADA or Na₂ADA and vanadium salt is substantially minimized, and the alkalinity or basicity of the solution is maintained. This process effectively avoids the need for acidification of the Stretford solution to destroy the thiosulfate, which would then require re-alkalizing; the re-alkalizing forms soluble salts of the acid used for acidification.

There are numerous patents relating to the Stretford process and to handling, using, or treating the Stretford solution, e.g., U.S. 2,997,439; U.S. 3,035,889; U.S. 3,097,926; U.S. 3,752,877; U.S. 3,904,734; U.S. 3,959,452; U.S. 3,975,508; U.S. 4,017,594; U.S. 4,118,467; U.S. 4,206,194; and European Patent Application Publ. No. 0 002 880 A3 having an Application Number 78300471.6 filed 09.10.78. The most relevant is believed to be U.S. 3,810,833, which is directed to conducting the process at an acidic pH, where the Stretford solution requires neutralization, as mentioned above, and has a very low solids content.

According to a first aspect of the present invention there is provided a process for treating a used, substantially sulfur particle - free Stretford process alkaline aqueous solution containing anthraquinone disulfonate ions and vanadate ions, the process comprising :

contacting the solution with activated carbon to separate anthraquinone disulfonate from the solution,

then contacting the solution with an anion exchange resin to separate the vanadate from the solution,

obtaining thereby an alkaline aqueous solution which is substantially depleted of the anthraquinone disulfonate and the vanadate.

The solution may contain disodium anthraquinone disulfonate and sodium vanadate as the anthraquinone disulfonate and vanadate ions and further contain sodium carbonate, sodium bicarbonate, sodium thiosulfate, sodium sulfate and sodium hydroxide.

In a second aspect the invention provides a process for controlling the amount of sodium thiosulfate and/or sodium sulfate in a mainstream Stretford process alkaline solution, the process comprising

contacting a portion of the Stretford solution, which portion is substantially free of sulfur particles, with activated carbon to substantially remove anthraquinone disulfonate therefrom,

- 4 -

then contacting the Stretford solution with an anion exchange resin to substantially remove vanadate therefrom,

5 following which the solution, now containing little or no anthraquinone disulfonate and containing little or no vanadate, but containing most, if not all, of the thiosulfate and/or sulfate is discarded from the anion exchange resin.

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It is preferred that the solution to be subjected to either of the above processes (i.e. the solution to be treated in the first aspect or the said portion of the second aspect) is separated from a mainstream used Stretford process liquid which contains sulfur particles, the sulfur particles being removed by filtration, for instance, so that there are no significant quantities of sulfur particles in the filtrate. The anthraquinone disulfonate ions and
15 vanadate ions may then be recovered from the activated carbon and the ion exchange resin and recycled to the mainstream for further use.

Ideally there should not be any particles
25 whatsoever in the solution, since if significant quantities of particles are present the activated carbon and the ion exchange resin require frequent back-washing to prevent plugging.

17

In a preferred embodiment a portion of an alkaline aqueous solution (viz. a "Stretford Solution") containing a salt of anthraquinone disulfonic acid (ADA), a vanadium salt, soluble alkalinities, sulfate values and thiosulfate values is separated as a side-stream from the sulfur particle-containing mainstream. The sidestream is contacted with activated charcoal which takes up the ADA from the solution, then is contacted with an anion exchange resin to take up the vanadium values from the solution, the thiosulfate and sulfate values substantially remaining with the solution. The ADA and vanadium values are recovered from the charcoal and exchange resin using an aqueous wash and are recycled to the Stretford solution for further use. An alkaline wash is used to regenerate the exchange resin.

The Stretford solution for use in the present invention is one which contains the requisite amount of ADA-salt (especially $\text{Na}_2\text{-ADA}$), of vanadium salt (especially sodium vanadate), of side products of the alkaline material (especially NaOH) used in maintaining the solution at a basic pH, and a sulfate and/or thiosulfate side-product (e.g. $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_4).

Ordinarily the amount of ADA-salt in the solution is maintained in the range of 1 to 5 gm/liter, though greater or lesser concentrations may sometimes be encountered. The preferred concentration is usually in the range of 1.5 to 3.0 gm/liter.

The amount of vanadium salt in the solution is usually in the range of 4 to 6 gm/liter, preferably 5.5 to 6.0 gm/liter, though greater or lesser concentrations may sometimes be encountered.

The amount of alkaline material (especially NaOH) employed to maintain the Stretford solution at a basic pH is somewhat dependent on the amount of acid or other reactants in a given volume of gas being treated.

- 5 The CO, CO₂, H₂S, SO₂, etc. reacts with the alkaline material to form salts. Thiosulfates are formed from NaHS and oxygen. Ordinarily there is an amount of alkaline material in the Stretford solution, including make-up amounts, sufficient to maintain an alkaline pH,
10 preferably a pH of 8.5 to 9.0.

- The temperature of the Stretford solution is principally determined by the amount of heat taken up from contact with the hot tail gases. Due to heat losses from the piping and equipment, the temperature
15 of the Stretford solution at the point in the process at which the present invention is preferably applied is still fairly warm, usually being in the range of 30°C to 40°C. The aqueous wash (which may be alkaline) used in regenerating the activated carbon may be at ambient temperature, but is
20 preferably in the range of 35°C to 100°C, most preferably at or near 100°C. The alkaline aqueous wash of the anion exchange resin may be at ambient temperature, and is preferably in the range of 35°C to 50°C. Higher temperatures may be used if the resin stability against
25 decomposition or degradation is not jeopardized by such higher temperatures. The water-eluted NaADA and Na₂ADA and alkaline material eluted vanadium salt from the activated carbon and exchange resin, respectively, are usually recycled back to the circulating Stretford
30 solution without adjustment of temperature. The anion exchange resin usually takes up an appreciable portion of any carbonate and bicarbonate ions in the Stretford solution and these are also washed out by the alkaline

material wash along with the vanadium salt and are also returned to the Stretford solution. In comparison with the cost of the NaADA or Na₂ADA and vanadium salt, the extraneous carbonate, bicarbonate, sulfate, thiosulfate, sulfur, and other such compounds have relatively little value.

During the washing of the NaADA or Na₂ADA loaded charcoal with water or alkaline material, e.g., NaOH, to wash out the NaAda or Na₂ADA, which is preferably done using very hot (up to 100°C) water or alkaline material, e.g., NaOH, there sometimes is a relatively small amount of sulfate, thiosulfate or other side-products from the Stretford solution which are also washed out of the activated carbon, but these are in tolerable amounts and may be re-cycled along with the ADA.

Washing of the anion exchange resin with alkaline material to wash out the vanadium compounds and regenerate the resin may be done at from ambient temperature to 100°C (if the resin will withstand hot alkaline material), but is preferably done at a temperature in the range of 30°C to 50°C. Conveniently, the regeneration is done with the alkaline material at a temperature closely approximating the temperature of the Stretford solution when it passes through the resin. The alkaline effluent from the wash cycle brings out the vanadium salt and usually contains tolerable amounts of the carbonate, bicarbonate and other side products of the Stretford solution which may have remained in the resin following the resin loading step. The alkaline material wash from the resin can be employed as the wash liquor for the activated carbon especially if heated to a temperature of up to 100°C.

- 8 -

The anion exchange resin may be any of the strong or weak base resins available for use as anion exchange resins, but preferably the resin is one of the strong base variety. Of the anion exchange resins available some are of the porous variety and some of the gel-type.

The activated carbon may be any of the commercially available finely-divided chars having activated, highly absorbent surfaces. By "activated carbon" and "chars" it is meant that any of the known activated carbon char materials derived from carbonaceous materials may be used.

NaOH is the preferred alkaline material to be used in the present invention, especially because it is readily available and relatively inexpensive, but other alkali metal hydroxides, such as KOH, may be used. If commercial grades of such alkalies are used which contain chloride impurities, these impurities may build up to a undesirable concentration unless steps are taken to limit the build-up. The present invention is beneficial with respect to chloride build-up in that while the process is effective in substantially removing sulfates and thiosulfates from the treated side-streams, it also substantially removes Cl^- ions at the same time. For instance, a sulfur particle-free portion of Stretford solution containing 3800 ppm Cl^- ion by weight (among its other ingredients) is passed through an activated carbon filter, then through an anion exchange bed, and the solution is found to still contain 3620 ppm Cl^- ion by weight, the solution at this point being purged from the system; thus over 95% of the Cl^- ion from the portion of Stretford solution is removed and not re-cycled.

21

In place of the preferred hot water or hot alkaline material wash for the activated carbon desorption step, one may use aqueous solutions containing inert organic compounds such as acetone or methylene chloride. For instance, it has been determined that water/acetone (3/1 volume ratio @ 34°C) and water/methylene chloride (3/1 volume ratio @ 34°C) can be used to recover NaADA or Na₂ADA from the activated carbon. This is beneficial as it allows regeneration of the activated carbon at relatively lower temperature, but it may be advisable to substantially remove the organic portion prior to recycle to the Stretford solution.

Example 1

A 700-ml. portion of Stretford solution is taken as a side-stream from an alkaline mainstream of Stretford solution containing dispersed particles of sulfur, a filter being used to keep the particulate sulfur in the mainstream. The side-stream of Stretford solution (34°C, pH 8.8) is passed through a column containing 120 ml of activated carbon, 12-40 mesh (1700-425 µm) and derived from bituminous coal, at 6.5 ml/min. The effluent is then passed through a 120 ml column of a strong base macroporous anion exchange resin (OH⁻ form, 20-50 mesh (850-300 µm)). The effluent from the resin is discarded.

Recovery of the Na₂ADA from the activated carbon is accomplished by passing 700 ml. of 100°C water (neutral pH) through the column at 6.5 ml/min. Recovery of sodium vanadate, sodium carbonate, and sodium bicarbonate from the resin is accomplished by passing 630 ml of 34°C aqueous sodium hydroxide (4% concentration) through the resin at 6.5 ml/min.

- 10 -

The following Table I indicates the approximate amounts of ADA, vanadate, sodium bicarbonate, sodium carbonate, sodium thiosulfate, and sodium sulfate to be found in the various solutions. Amounts shown are in
5 gms. per liter.

TABLE I

	<u>Identity of Solution</u>	<u>ADA</u>	<u>Per Cycle Analysis of Solutions</u>				
			<u>V¹</u>	<u>Bicarb.²</u>	<u>Carb.³</u>	<u>Thio⁴</u>	<u>Sulf.⁵</u>
10	Stretford, at the start ...	1.87	6.0	4	7	310	28
	Stretford, after carbon ...	0.04	5.8	3	7	285	28
	Aq. eluate from carbon ...	1.85	0	0	0	0	2
15	Stretford, after resin ...	0	0.8	2	3	260	26
	Alkaline eluate from resin ...	0	6.3	5	40	20	0
20	¹ vanadate; ² bicarbonate; ³ carbonate; ⁴ thiosulfate; ⁵ sulfate						

By calculation, the recovery of ADA is about 96% and recovery of vanadate is about 94%. The sulfate and thiosulfate compounds are substantially retained in the discarded effluent.

25 Example 2

A material balance is made by accounting for the ingredients in the recovery stream and the waste (purge) stream and comparing with ingredients used in the feed solution and the regeneration solution.

- 11 -

The feed solution (i.e. the beginning Stretford solution) during the material balance monitoring contains (all quantities being parts by weight):

5	H ₂ O	38,724.0
	Alkalinity	373.4
	NaVO ₃	225.8
	ADA	83.8
	Na ₂ S ₂ O ₃ (as the pentahydrate) .	11,853.0
	Na ₂ SO ₄	1,064.0

10 The regeneration solution employed during the monitoring comprises:

	H ₂ O	59,803.8
	NaOH	625.4

15 The above quantities represent the total amounts into the process. The total amounts out of the process are represented by the amounts in the purge (waste stream) and the recovery stream (for use as recycle).

The purge during the monitoring is:

20	NaOH	267.8
	H ₂ O	38,724.0
	Alkalinity	260.5
	NaVO ₃	34.7
	ADA	0
25	Na ₂ S ₂ O ₃ (as the pentahydrate)..	11,289.0
	Na ₂ SO ₄	988.0

- 12 -

The recovery during the monitoring is:

	NaOH	357.6
	H ₂ O	59,803.8
	Alkalinity	112.8
5	NaVO ₃	191.1
	ADA	83.8
	Na ₂ S ₂ O ₃ (as the pentahydrate).	564.0
	Na ₂ SO ₄	76.0

From the above figures the amount of recovery
10 of ADA, NaVO₃, alkalinity, and NaOH is about:

ADA	100%	Alkalinity	30.2%
NaVO ₃	84.6%	NaOH	57.2%
Na ₂ S ₂ O ₃ · 5H ₂ O	4.8%	NaSO ₄	7.1%

The amounts in the purge are about:

15	Na ₂ S ₂ O ₃ · 5H ₂ O	95.2%	Alkalinity	69.8%
	NaVO ₃	15.4%	NaOH	42.8%
	Na ₂ SO ₄	92.9%		

In the above ingredients the term "alkalinity"
is used to account for compounds which have formed
20 salts with the NaOH during the tail gas scrubbing
operation using the alkaline Stretford solution, such
as sodium carbonate and sodium bicarbonate, but the
sodium thiosulfate and sodium sulfate are treated as
separate items.

~~Enclosed herein by reference is the monitoring
application, USBN 300,035, a copy of which is filed
herewith.~~

CLAIMS:

1. A process for treating a used, substantially sulfur particle-free, Stretford process alkaline aqueous solution containing anthraquinone disulfonate ions and vanadate ions, the process comprising:

contacting the solution with activated carbon to separate anthraquinone disulfonate from the solution,

then contacting the solution with an anion exchange resin to separate the vanadate from the solution,

obtaining thereby an alkaline aqueous solution which is substantially depleted of the anthraquinone disulfonate and the vanadate.

2. A process as claimed in claim 1 wherein the solution to be treated is substantially free of any particles.

3. A process as claimed in claim 1 or claim 2 wherein the solution to be treated is separated from a used Stretford process liquid containing sulfur particles.

4. A process for controlling the amount of sodium thiosulfate and/or sodium sulfate in a mainstream Stretford process alkaline solution, the process comprising



contacting a portion of the Stretford solution, which portion is substantially free of sulfur particles, with activated carbon to substantially remove anthraquinone disulfonate therefrom,

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then contacting the Stretford solution with an anion exchange resin to substantially remove vanadate therefrom,

10 following which the solution, now containing little or no anthraquinone disulfonate and containing little or no vanadate, but containing most, if not all, of the thiosulfate and/or sulfate is discarded from the anion exchange resin.

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5. A process as claimed in any one of the preceding claims wherein the Stretford process alkaline aqueous solution contains disodium anthraquinone disulfonate and sodium vanadate as the anthraquinone disulfonate
20 and vanadate ions, and further contains sodium carbonate, sodium bicarbonate, sodium thiosulfate, sodium sulfate and sodium hydroxide.

6. A process as claimed in claim 4 or claim 5
25 wherein the used Stretford process liquid from which the portion is separated contains sulfur particles.

7. A process as claimed in any one of claims 4 to 6 wherein the said portion is substantially
30 free of any particles.

8. A process as claimed in any one of the preceding claims wherein the carbon is regenerated



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by using an aqueous wash to elute the anthraquinone disulfonate.

9. A process as claimed in claim 8 wherein the aqueous wash has a temperature in the range of from 35°C to 100°C.

10. A process as claimed in claim 9 wherein the temperature is substantially 100°C.

11. A process as claimed in any one of claims 8 to 10 wherein the aqueous wash is alkaline.

12. A process as claimed in any one of the preceding claims wherein the anion exchange resin is regenerated by using an alkaline aqueous wash to elute the vanadate.

13. A process as claimed in claim 12 wherein the alkaline aqueous wash has a temperature in the range of from 35°C to 100°C.

14. A process as claimed in claim 13 wherein the temperature is in the range of from 35°C to 50°C.

15. A process as claimed in any one of claims 4 to 7 wherein the anthraquinone disulfonate is eluted from the carbon by a process as defined in any one of claims 8 to 11 and the vanadate is eluted from the anion exchange resin by a process as defined in any one of claims 12 to 14, and the so-recovered anthraquinone disulfonate and vanadate are recycled back to the Stretford process liquid.



16. A process as claimed in claim 15 wherein the anthraquinone disulfonate is eluted by a process as claimed in claim 11 and the alkaline aqueous wash from the anion exchange resin is then used
5 to elute the anthraquinone disulfonate from the activated carbon.

17. A process as claimed in claim 16 wherein the wash is caustic solution.
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18. A process as claimed in claim 1 or claim 4 substantially as hereinbefore described in Example 1 or Example 2.



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