PATENT SPECIFICATION (11) 1 584 198

1 584 198

(21) Application No. 34007/77 (22) Filed 12 Aug. 1977
(31) Convention Application No. 716 525
(32) Filed 23 Aug. 1976 in
(33) United States of America (US)
(44) Complete Specification published 11 Feb. 1981
(51) INT CL³ C02F 1/52
(52) Index at acceptance C1C 217 230 304 322 400 40Y B



(54) SUSPENDED CARBON SEPARATION

(71) I, FRANCIS CLYDE PETERSEN, a citizen of the United States of America, of 26801 Via Victoria, Mission Viejo, California, United States of America do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for recovering suspended carbon from an aqueous medium. The suspended carbon is in the form of extremely fine particles, i.e. near colloidal and colloidal particles. A ferrous salt is added to the medium in an amount sufficient to agglomerate the suspended carbon.

In recent years, the separation of materials from various streams and the recycling of both the separated materials and the stream itself has become of great importance with the increasing emphasis on conservation of existing natural resources. The use of an aqueous medium to transport coal for subsequent use in coal burning (or coal utilizing) processes has also become important. The coal must be separated from the aqueous medium. The basic separation involves existing technology. However, there usually remain finely divided carbon particles in the aqueous medium, which particulate matter is colloidal or near-colloidal in size. Separation of this remaining suspended carbon has presented great difficulties.

A distinction should be noted here between two problems in clarifying and purifying an aqueous medium for reuse. One problem is the removal of dissolved materials from the liquid. This usually involves steps of crystalization and precipitation. The steps utilized are of the following four steps: supersaturation by cooling; supersaturation by the evaporation of the solvent; supersaturation by adiabatic evaporations; and salting out by adding a more soluable material to the solvent that will shift the driving force reducing the soluability of the substance in question causing it to crystalize and precipitate out.

The technology involved in this type of process is quite different from that involved in agglomerating and flocculating finely divided solid matter from a liquid. It is to the latter problem that the present invention is directed.

The agglomeration and flocculation of finely divided suspended solid materials in the past has involved using a material such as lime for an initial agglomeration followed by use of a water soluable organic polymeric flocculant to complete the process. Particulate carbon has been an extremely difficult material to separate. The amount of lime required and the amount of organic polymeric flocculant that have been required to remove particulate carbon has tended to make the process quite costly when possible at all. Accordingly a need has developed for a more efficient agglomerating agent which can improve the efficiency of the entire agglomeration/flocculation process.

The present invention provides a process for recovering supended carbon from an aqueous medium which has not previously been treated with an anionic polymer for suspended carbon removal which comprises adding a ferrous salt to the medium in an amount sufficient to agglomerate the suspended carbon.

The ferrous salt is preferably selected from ferrous chloride and ferrous sulfate. For many uses, this may be all that is necessary. However, the process can be further improved by flocculating the aqueous medium with a water soluable organic polymeric flocculant. Due to the efficiency of the ferrous salt as an agglomerating agent normally no pH adjustment will be necessary, however, the flocculating step is improved if the pH of the aqueous medium is adjusted to at least about 7 prior to the ffocculating step. If ferrous chloride is used, it is most desirably added to the aqueous medium in the form of a thirty percent (30%) aqueous

solution of ferrous chloride. If ferrous sulphate is used it may be added in the form of a 1.22 specific gravity solution.

The function of the agglomerating agent or, as it may also be called, primary coagulants, is believed to be a breaking up of emulsions that have formed and further, the formation of pinpoint flocs with particulate matter that is colloidal or near-colloidal in the water and finally, by use thereof, a reduction in the demand for the organic polymeric flocculant, typically an anionic polymer such as polyacrylamide polymer for adequate flocculation. It has been discovered that ferrous salts, particularly a ferrous salt selected from ferrous chloride and ferrous sulfate, are substantially better than the known agglomerating agents or primary coagulants, such as ferric chloride and the like which are quite ineffective in agglomerating particulate carbon. Exactly why this is true is not entirely understood at this time. A series of tests were run to determine the effectiveness of ferrous chloride and ferrous sulfate as agglomerates in the recovery of suspended carbon from aqueous media. The procedure that was followed in these tests was to fix the anionic polymer concentration for the flocculation step, then vary the amount of ferrous salt added for the initial agglomeration to the minimum necessary to get a clear supernatant, and then adjust the ferrous salt concentration to minimize the requirement for the anionic polymer. This is similar to what would have to be done in commercial operations as the concentration of fines in a coal slurry stream would be constantly changing.

The results of the tests are shown in Table 1.

TABLE I

Sample	pH	$FeCl_2$ (30% solu.)	Anionic Polymer
A	7–7.5	3 ppm	1–2 ppm
B	5 initially – 7 for polymer add	0.5 cc/500 cc (7% solids) solu.	0.02 g/500 cc
C	7.5	0.5 cc/500 cc (40% solids) solu.	0.0075 g/500 cc
D	8	0.5 cc/500 cc (2.77% solids) solu.	0.0025 g/500 cc
E	8	0.75 cc/500 cc (2.77% solids) solu. of 1.22 s.g. $FeSO_4$	0.0025 g/500 cc

Sample A was a coke-water stream coming off a flasher from a system for removing coke from water. As indicated therein, with the pH running normally between 7 and 7.5, three parts per million ferrous chloride was the optimum agglomerate concentration with a resultant one to two parts per million requirement for anionic polymer, the polymer being used as the flocculant being that known in the trade as Allied Colloids Percol 156 which is a polyacrylamide polymer. Sample B was a sample from a concentrate coming out of centrifuges used in separating particulate coal material from a coal slurry transport system. This material was therefore coal fines. The ferrous chloride-anionic polymer 2 step procedure worked at a pH as low as 5, however, it was found by raising the pH to 7 and above after agglomeration, the polymer demand was decreased to a minimum. As indicated in the table, 0.5cc of a 30% solution of ferrous chloride with 500cc of solution containing 7.5% solids, resulted in an anionic polymer requirement of 0.02g per 500cc. The anionic polymer that worked best, again, was a polyacrylamide polymer, either that known in the trade as Allied Colloids Percol 156 or that known in the trade as Calgon WT 2900 (Registered Trade Mark). Sample C was a high ash coal wash stream containing 40% solids. No pH adjustment was necessary as the normal pH of the stream was 7.5. Again, 0.5cc of 30% ferrous chloride per 500cc of solution containing 40% solids

resulted in an anionic polymer requirement of 0.0075g per 500cc. The anionic polymer used was that known in the trade as Calgon WT 2900. Sample runs D and E both relate to agglomeration and flocculation of an aqueous medium containing coarse fines from a coal washing operation. Sample runs D relate to the use of ferrous chloride according to the present invention while sample runs E relate to the use of ferrous sulfate in the form of a 1.22 specific gravity solution as the agglomerate. The anionic polymer used in the subsequent flocculation step in both cases was Calgon WT 2900 (RTM). As shown by these sample runs, in order to utilize the same amount of anionic polymer in the flocculating step, 0.0025g per 500cc, one would have to use 50% more ferrous sulfate (0.75cc per 500cc of solution) than of ferrous chloride (0.5cc per 500cc solution). The pH of the solution in both cases is normally 8 and no adjustment was required.

Analysis of the suspended particulate carbon in the same aqueous medium as for sample runs D and E showed a majority of the suspended fines are 50 microns or less in size with a high percentage in the range of 0.5 microns. The coal being washed is a low sulfur fuel which varies in composition radically from one hour to the next due to degrees of oxidation of the coal deposit. This variation in coal quality causes comparable variations in the amounts of agglomerate and flocculant required to separate the fines.

When using lime as the agglomerate, the polymer dosage required can change within one hour from as low as 5 parts per million (ppm) to as high as 20 ppm. Using instead a reasonably steady amount of ferrous chloride, i.e. between 0.2 pounds per 1000 pounds of feed to 0.26 pounds per 1000 pounds of feed, the polymer demand has fallen between 1.5 ppm and 8 ppm. The amount of solids in the aqueous medium ranged up to 5.2%.

A series of tests were run on the aqueous medium of sample run B wherein the amount of solids was about 7.8%, using ferric chloride, aluminum sulfate (alum), and sodium aluminate as agglomerates. The initial pH was 5.5. In separate tests up to 1 gram on an anhydrous basis of each was added to 1000cc of sample with no noticable effect. In each test the pH was then adjusted to 8 by adding sodium hydroxide. Anionic polymer was then added and no flocculation was detected.

The sequence of operations, the use of the primary coagulant or agglomerate, followed in a second step, after any necessary pH adjustment, with the addition of a flocculant, can be carried out in any conventional separation apparatus. Desirably, the flocculation separation step is accomplished with a centrifuge and the anionic polyacrylamide which is a water soluable polymer is introduced into the feed stream of the centrifuge. This minimizes any problems due to shearing action in the centrifuge.

While there have been shown and described hereinabove possible embodiments of the invention, it is to be understood the invention is not limited thereto and that various changes, alterations, and modifications can be made thereto without departing from the scope of the appended claims.

WHAT I CLAIM IS:—

1. A process for recovering suspended carbon from an aqueous medium which has not previously been treated with an anionic polymer for suspended carbon removal which comprises adding a ferrous salt to the medium in an amount sufficient to agglomerate the suspended carbon.

2. The process of claim 1 wherein the ferrous salt is selected from ferrous chloride and ferrous sulfate.

3. The process of claim 1 including the additional step of flocculating the aqueous medium with a water soluble organic polymeric flocculant after the agglomeration with a ferrous salt.

4. The process of claim 3 wherein the pH of the aqueous medium is adjusted to at least about 7 prior to the flocculating step.

5. The process of any of the preceding claims, wherein the salt is ferrous chloride.

6. The process of claim 5 wherein the ferrous chloride is added in the form of a 30% aqueous solution of ferrous chloride.

7. The process of any of the preceding claims 1 to 4, wherein the salt is ferrous sulfate.

8. The process of claim 7 wherein the ferrous sulfate is added in the form of a 1.22 specific gravity solution.

9. A process for recovering suspended carbon from an aqueous medium substantially or herein described.

LANGNER PARRY,
High Holborn House,
52—54 High Holborn,
London, WC1V 6RR.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.