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PRECIPITATION OF HYDROUS VANADIUM
OXIDE

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This invention relates to a new and useful method of precipitating vanadium compounds. It relates in particular to an improved process for the substantially complete hydrolysis of soluble vanadate into high quality, easily processed hydrous vanadium oxide.

In the practice of the art of vanadium recovery, vanadium-containing ores and residues which have been previously ground, and which are to be processed for their vanadium content, are often roasted with sodium salts to convert the vanadium values to water-soluble compounds, specifically, sodium vanadates, which are extracted in a subsequent leaching operation. The hydrolysis of the resulting leach liquor by neutralization with acid accompanied by heating is an established procedure in the art of precipitating out the vanadium in the form of a filterable hydrous oxide. Yet certain obstacles have not heretofore been adequately overcome in hydrolyzing vanadium from such solutions. The present invention springs from a search for adequate means of overcoming the hindrance encountered in these imperfect steps of this procedure. The advantageous features of the method of the present invention, in addition to rapidly giving a high recovery of vanadium in a state of relatively high purity, lie in its avoidance of certain well-known difficulties accruing from the tendency of the precipitate to form viscid, gummy flocs which adhere to the hydrolyzing apparatus, thus interfering with normal hydrolysis and preventing easy handling and washing of the precipitate and easy cleaning of the apparatus and equipment.

The phenomenon of sticking and adherence of the precipitated hydrous vanadium oxide flocs to the inside walls and other parts of the precipitating apparatus, such as coils and agitator, is invariably encountered when the required (calculated) amount of acid is added directly to the entire sodium vanadate solution under agitation, or in a manner which causes immediate mixing of the entire quantities of the two liquors. This sticking is encountered whether the contact surface is made of ceramics, bricks, glass, or of suitably resistant metals or alloys.

It has now been found, that the difficulties of sticking and adherence of the hydrous vanadium oxide precipitate heretofore encountered in the art may be easily overcome according to the present invention by the simple expedient of a two-step mixing in which all of the required acid is first introduced to a minor amount of vanadate liquor causing at least a partial permanent pre-

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cipitation of nuclear hydrous vanadium oxide. This acid nuclear composition is later mixed with the additional vanadate liquor to obtain easily filterable, non-gummy and non-sticky precipitate of hydrous vanadium oxide.

Accordingly, it is the primary object of the present invention to provide a method for obtaining by hydrolysis of vanadate solutions, particularly solutions of alkali metal vanadates, easily filterable, non-sticky precipitates of hydrous vanadium oxide. This and other objects will become apparent from the following description.

Sodium vanadate liquors which are obtained by direct leaching of alkali-treated ores or materials poor in vanadium are low in vanadium content. While the concentration of the vanadate liquor is not critical to the non-sticking hydrolysis method of this invention, best results are obtained with solutions of fairly high vanadium content. Thus we have found that solutions upward of 10 grams of vanadium per liter and preferably higher are more satisfactory than more dilute solutions. Such concentrated solutions may be obtained by counter-current leaching of the alkali-roasted materials, and if necessary, by subsequent further concentration by evaporation.

Hydrous vanadium oxide is soluble under both acid and alkaline conditions, and the problem of complete precipitation of the vanadium values is a matter of establishing the correct pH in the solution. Experiments have shown that by neutralizing with acid, preferably a mineral acid, to a pH of 2.0-3.0, preferably 2.5, which must be maintained, substantially complete hydrolysis is obtained. Higher or lower pH will give incomplete or no precipitation of vanadium. On the other hand, reduction of the pH of a minor amount of vanadate liquor to substantially below 2.5, by the initial addition of a large quantity of acid, will produce a condition of partial precipitation of hydrous vanadium oxide which will function as nucleating material when added to a larger quantity of vanadate liquor, in an amount sufficient to produce after final mixing an optimum pH of 2.0-3.0, preferably 2.5.

It has also been found that high concentration of salts, such as alkali metal, chloride and/or sulfate, to a certain degree will suppress the solubility of the hydrous vanadium oxide and thereby aid in its complete recovery.

Broadly the present invention comprises three steps: (a) acidification of an amount of the vanadate liquor, by addition of sufficient acid to reduce the pH considerably below 2.5 (the re-

sulting partial precipitation of hydrous vanadium oxide serves as nuclei in the second step of the process); (b) complete neutralization, to a pH of 2.0 to 3.0, preferably 2.5, by mixing the highly acid nucleating liquor with additional sodium vanadate liquor; (c) heating to complete precipitation.

More specifically the present process consists of bringing together in a vessel an amount of sodium vanadate liquor with a large excess of mineral acid followed by mixing with an additional amount of vanadate liquor calculated theoretically, to produce in the final mix a pH of about 2.5. In a preferred embodiment of the present invention, the vanadate solution is divided, prior to the acid addition, into two portions. One portion, comprising 10-45% of the original amount, is ready for mixing with the acid. The remaining portion is set aside for later use. Into the first portion of the liquor is poured the entire amount of acid prepared to neutralize the whole body of vanadate liquor. The temperature of addition may vary widely, but will usually be between 20° to 80° C. It is most likely that the liquor to be used will be run fresh from the counter-current leaching process, in which case its temperature will be found near 80° C. Preferably, therefore, the process of the present invention is operated with liquors having a relatively high temperature at the time of neutralization. Such practice obviates the uneconomical cooling and reheating, with its demand for extra fuel and extra time. However, if, for any reason, it becomes necessary to store the leach liquor for some time prior to hydrolysis the addition of acid may begin simultaneously with the reheating, without danger of ultimate sticking and loss in vanadium recovery.

The mixture of a portion of the vanadate liquor with the rather large amount of calculated total acid yields a dilute acid solution in which, as the mixing proceeds, large flocs of V_2O_5 precipitate out, forming what are hereinafter referred to as "nuclei," since they appear to facilitate further precipitation when mixed with the remaining portion of the vanadate liquor.

A substantial redissolution or dispersion of the initially precipitated hydrous vanadium oxide in the excess acid does not destroy the nuclear potency.

After the excess acid mixes thoroughly with the first portion of the alkaline vanadate liquor, the resulting dilute acid mixture, containing precipitated nuclei, is slowly added to the remaining second portion of the vanadate liquor, the mixture undergoing slow agitation during the entire period of addition to bring all parts of the alkaline vanadate in contact with the acid and the nuclei. Although the addition time may be shortened to as little as eight minutes, best results are achieved by slowing it to cover at least fifteen minutes, and preferably from 20 to 60 minutes. Meanwhile, reaction between alkaline solution and acid raises the temperature 3° to 5° C., or from approximately 80° to near 85° C.

Simultaneously, the mixture is heated by external means to raise the temperature some 10° over a period of one hour, to give a total final temperature of 95° C. Boiling is not necessary, but may be employed to complete hydrolysis. The V_2O_5 will be virtually all precipitated in excellent non-gummy, filterable condition. The precipitate will be of moderate volume and no film will remain on equipment. Over 99% of

the vanadium in the leach liquor will be found in the precipitate.

The following example illustrates a preferred embodiment of the invention:

200 liters of vanadate liquor at 80° C., of pH=9.0, containing 15 grams of vanadium per liter as sodium vanadate and 6 grams per liter of sodium carbonate were separated into two parts by volume, one representing 10% or 20 liters, the other, 90% or 180 liters. The larger portion was run into a Haveg tank equipped with Haveg sweep agitators. There, while waiting for further treatment, it was slowly agitated. The other portion representing 10% was mixed directly into a similar tank holding a quantity of 62% H_2SO_4 previously determined by titration of a small sample of the vanadate liquor to be sufficient to neutralize the entire 200 liters of leach liquor to a pH of 2.5. The temperature of the acid as well as that of the vanadate liquor was 80° C. at the time of mixing. Under the high acid content and slow agitation there was formed in the 20 liters of vanadate liquor a certain amount of precipitate which at least in part persisted and remained in suspension in the acid liquor. This acid mixture was poured directly but slowly with agitation into the 180 liters of vanadate liquor within the space of 15 minutes. Heat of reaction between acid and alkaline liquor, as well as outside heating by means of Karbate bayonet heaters using 5 lb. steam, brought the temperature to 95° C. in one hour, at which time 99.1% of the vanadium was precipitated. The slow addition with stirring permitted the acid to react intimately with all parts of the vanadate liquor and allowed a not too violent liberation of the CO_2 gas to occur. As a result, the flocs built into a non-gummy, non-sticking, easily filterable and washable, substantially pure precipitate.

When repeating the example, but adding the calculated amount of sulfuric acid directly to the total amount of sodium vanadate liquor, a sticky precipitate formed which adhered to the walls of the apparatus, to the coils, and to the agitator shaft and blades. This precipitate was difficult to remove and did not filter or wash easily. The final product was also less pure than that obtained by the process of this invention.

We claim:

1. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises, admixing with a solution of mineral acid an amount of alkali metal vanadate solution consisting of from about 10% to about 45% of that required to neutralize said mineral acid solution, thereby to form a hydrous vanadium oxide nuclear composition, and adding said nuclear composition to additional alkali metal vanadate solution meanwhile agitating, said additional alkali metal vanadate solution being in amount sufficient to neutralize said nuclear composition to a pH of from about 2 to about 3, agitating and heating the whole at a temperature from 75° to boiling until the vanadium content of the mixture is substantially completely precipitated as hydrous vanadium oxide.

2. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises, admixing with a solution of sulphuric acid an amount of alkali metal vanadate solution consisting of from about 10% to about 45% of that required to neutralize said sulphuric acid solution, thereby to form a hydrous vanadium oxide nuclear compo-

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sition, and adding said nuclear composition to additional alkali metal vanadate solution meanwhile agitating, said additional alkali metal vanadate solution being in amount sufficient to neutralize said nuclear composition to a pH of from about 2 to about 3, agitating and heating the whole at a temperature from 75° to boiling until the vanadium content of the mixture is substantially completely precipitated as hydrous vanadium oxide.

3. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises, admixing with a solution of mineral acid an amount of alkali metal vanadate solution consisting of from about 10% to about 45% of that required to neutralize said mineral acid solution, thereby to form a hydrous vanadium oxide nuclear composition, and adding and simultaneously mixing said nuclear composition over a period of from 8 minutes to one hour, to additional alkali metal vanadate solution, said additional alkali metal vanadate solution being in amount sufficient to neutralize said nuclear composition to a pH of from about 2 to about 3, agitating and heating the whole at a temperature from 75° to boiling until the vanadium content of the mixture is substantially completely precipitated as hydrous vanadium oxide.

4. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises, admixing with a solution of mineral acid an amount of alkali metal vanadate solution consisting of from about 10% to about 45% of that required to neutralize said mineral acid solution, thereby to form a hydrous vanadium oxide nuclear composition, and adding and simultaneously mixing said nuclear composition over a period of about 15 minutes, to additional alkali metal vanadate solution, said additional alkali metal vanadate solution being in amount sufficient to neutralize said nuclear composition to a pH of from about 2 to about 3, agitating and heating the whole at a temperature from 75° to boiling until the vanadium content of the mixture is substantially completely precipitated as hydrous vanadium oxide.

5. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises, separating said vanadate solution into a major part and a minor part consisting of from about 10% to about 45% of the whole, admixing said minor part with a solution of sulphuric acid of sufficient strength to neutralize substantially the whole of said vanadate solution to a pH of from 2 to 3, thereby to form a hydrous vanadium oxide nuclear composi-

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tion, and adding and simultaneously mixing said nuclear composition with said major part of said vanadate solution over a period of from 8 minutes to one hour, agitating and heating at a temperature of from 75° C. to boiling for a length of time sufficient to precipitate substantially the entire vanadium content of said vanadate solution as hydrous vanadium oxide.

6. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises, separating said vanadate solution into a major part and a minor part consisting of from about 10% to about 45% of the whole, admixing said minor part with a solution of a mineral acid of sufficient strength to neutralize substantially the whole of said vanadate solution to a pH of from 2 to 3, thereby to form a hydrous vanadium oxide nuclear composition and adding and simultaneously mixing said nuclear composition with said major part of said vanadate solution, agitating and heating the whole at a temperature of from 75° C. to boiling for a length of time sufficient to precipitate substantially the entire vanadium content of said vanadate solution as hydrous vanadium oxide.

7. A process for preparing easily filterable hydrous vanadium oxide from an alkali metal vanadate solution which comprises admixing with a solution of sulphuric acid an amount of alkali metal vanadate solution consisting of from about 10% to about 45% of that required to neutralize said sulphuric solution, thereby to form a hydrous vanadium oxide composition and slowly adding and simultaneously mixing said nuclear composition to additional alkali metal vanadate solution, said additional alkali metal vanadate solution being in amount sufficient to neutralize said nuclei containing solution to a pH of from about 2 to about 3.

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