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REMOVAL OF CARBONACEOUS DEPOSITS

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The present invention relates to a method for removing undesirable carbonaceous deposits and more particularly to a method for removing acidic carbonaceous deposits from heating tubes and the like.

In numerous industrial processes, carbon containing materials are treated by heating or in other ways in a manner conducive to the formation of coke or similar carbonaceous deposits upon various surfaces within the treating equipment. These deposits are almost invariably objectionable and in many instances deleterious. In the past it has been common practice to remove carbonaceous deposits of this nature mechanically, i. e., either by means of special cutting equipment which may be inserted into the equipment which it is desired to clean or by partially dismantling the equipment to gain access to the parts which are coated. Mechanical cleaning procedure for the removal of carbonaceous deposits is, however, excessively time consuming and necessitates long and undesirable periods of inoperation of the equipment during cleaning. Further, there is the constant danger of damage to the equipment by mechanical cleaners or during the dismantling and reassembling operations.

Attempts have also been made to clean surfaces upon which carbonaceous deposits occur by other than mechanical means, as for example by burning the carbon out with an oxygen stream or by treating the carbonaceous deposits with strong chemical reagents which will convert the carbon to carbon dioxide. These methods have also been found to be generally undesirable due to ineffective removal of the objectionable deposits, attack on the metal parts by the chemical reagents or as a result of damage to the equipment as a consequence of overheating during the burning operation.

It is an object of the present invention to provide a method for rapidly and effectively removing carbonaceous deposits from surfaces to which they are adhering. Another object is to provide a method for carrying out the removal of such deposits without necessitating dismantling of equipment which may contain internal deposits. A further object is to provide a method for removing carbonaceous deposits from the interior surfaces of equipment in a form suitable for facile removal from the equipment and without danger of damage to the surfaces of the equipment. Still another object is to provide a method for removing carbonaceous deposits from surfaces to which they are adhering by gas generation

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within the interstices of the carbonaceous deposits. Other objects, together with some of the advantages to be derived in utilizing the present invention, will become apparent from the following detailed description.

According to the present invention, it has been found that carbonaceous deposits may be removed from surfaces to which they are adhering by generating carbon dioxide gas within the interstices of the coating. This may be generally brought about by reaction between an aqueous carbonate solution and an aqueous acid solution within the interstices of the carbonaceous deposit, preferably by first impregnating the deposit with an acid solution and then with a carbonate solution.

For purposes of illustration, the invention will be described with reference to the removal of carbonaceous deposits from the heating tubes of an acid concentrator. The conventional acid concentrator comprises a large steel container near the bottom of which are disposed heating coils through which steam or hot oil may be passed. When concentrating certain types of dilute acid, as for example spent sulfuric acid derived from petroleum refining processes, the organic impurities contained in the acid carbonize and a thin film of carbon is deposited on the heating tubes. The laminated deposit which is gradually built up as successive batches of acid are concentrated eventually attains sufficient thickness to seriously interfere with the heat transfer through the heating tubes. The conventional method of cleaning the carbonaceous deposits from these tubes involves removal of the tubes and scraping and requires that the concentrator be out of operation for a period of at least approximately 24 hours.

The following procedure was carried out in lieu of the dismantling and scraping operations. The concentrator was drained and 600 gallons of water introduced as a flushing medium to remove accumulations of acid on the floor of the concentrator. The flushing water was then drained out and approximately 7000 gallons of an aqueous solution containing approximately 5% by weight of sodium bicarbonate introduced, filling the concentrator to a level about 10 inches above the heating tubes. The bicarbonate solution was heated to and maintained at the boiling point for approximately 30 minutes, after which it was drained and the bottom of the concentrator again flushed with approximately 600 gallons of water. The concentrator was then charged with spent sulfuric acid and the heat transfer rate was

found to be as good as when the concentrator was first used. The total time required for the described cleaning procedure was less than 4 hours. Upon examination, it was found that the carbonaceous deposits had been completely removed from the tubes.

In the above example the carbonaceous deposits were, of course, impregnated with acid as rapidly as they formed. However, in those instances wherein a neutral deposit is encountered, an acid treatment should be applied before subjecting the deposits to the action of the carbonate solution. Alternatively, the neutral deposit may be first impregnated with a carbonate solution and then subjected to the action of an acid stronger than carbonic acid. In either case, it appears that the resulting reaction between the acidic and carbonate solutions produces carbon dioxide within the interstices of the carbonaceous deposits and the carbon dioxide breaks off the carbonaceous deposits from beneath in escaping. It will thus be apparent that any combination may be utilized which will react to yield carbon dioxide.

Particularly suitable sources of carbon dioxide for the purposes of the present invention are aqueous solutions of the inorganic alkali carbonates, e. g., sodium, potassium and ammonium carbonates and bi-carbonates. These compounds are preferred because of their relatively great solubility in water. However, other less water soluble inorganic carbonates may be employed under special conditions, as for example, the solubility of many inorganic carbonates in water may be substantially increased by passing carbon dioxide gas through the water while dissolving the carbonate. Also, in those instances wherein pressure tight equipment is to be cleaned, most inorganic carbonates may be employed and their solubility in water greatly increased by maintaining an atmosphere of carbon dioxide under pressure over the carbonate solution. Examples of specific compounds which may be employed in solution under conditions described above are the carbonates of lithium, beryllium, magnesium, calcium, barium, zinc, lead, manganese, silver, etc. In many instances it will also be found satisfactory to employ slurrys or suspensions of the more insoluble carbonates in water, or alternatively, alcoholic solutions, slurrys or suspensions of these compounds.

Any acid preferably in dilute aqueous solution which is stronger than carbonic acid and which will react with the carbonates to produce carbon dioxide may be utilized, as for example aqueous solutions of sulfuric, selenious, hydrochloric, hydrobromic, iodic, nitric, phosphoric, formic, acetic, lactic, oxalic, citric, etc. acids. Those acids weaker than acetic acid, i. e. acids having a dissociation constant less than approximately 10^{-5}, are generally unsatisfactory for the purposes of the invention since the amount of carbon dioxide formed during the reaction with carbonates is usually insufficient to exceed the solubility of carbon dioxide in water.

It will be apparent that the process may be applied in its principles to the removal of any porous carbonaceous deposits from any surfaces to which they may be adhering. If other materials are present in the carbonaceous deposits which will react unfavorably with carbonate or dilute acid solutions, they should be removed by flushing with water or another suitable solvent before the acid or carbonate solution is introduced. Improved impregnation of the carbonaceous deposits is obtained if the deposits are covered with the impregnating solution in a closed container which may be partially evacuated. However, in cases where such procedure is impractical or undesirable for one reason or another, satisfactory results are obtained, although over a somewhat longer period of time, by simply soaking the carbonaceous deposits in the impregnating solutions. Heating the solution during the reaction between the acid and the carbonate will, of course, increase the rate at which the undesirable deposit is removed since the carbon dioxide will be generated at a greater rate.

According to preferred procedure, the carbonaceous deposit which it is desired to remove is first subjected to the action of a dilute acid solution, as for example aqueous sulfuric acid having a concentration between about 20% and 60% by weight H_2SO_4, for a period of approximately one half hour. The concentration of the acid is not critical, however, and any convenient concentration may be employed. Shorter impregnation time may also be employed if it is feasible to carry out the impregnation under reduced pressure. The acid is then drained out of the system and a dilute solution of sodium acid carbonate substituted. The concentration of the carbonate solution may also be selected as a matter of convenience, although there appears to be no advantage in utilizing carbonate solutions having a concentration appreciably in excess of 10% by weight. Heat is preferably applied during the reaction between the acid and the carbonate in the interstices of the carbonaceous deposit. The carbonate solution is then drained out of the system and the procedure above repeated in those instances where the deposit is not entirely removed during the first treatment. After complete removal of the undesirable deposit, the system is flushed with water and is ready for use again. The reagents may both be stored, after filtration of the carbonaceous matter from the carbonate solution, and reused until exhausted.

The procedure outlined above wherein the carbonaceous deposits are first impregnated with acid and then with a carbonate solution is generally preferred in order to minimize possible attack by the acid on metal surfaces to which the deposits may be adhering during the reaction period, which is usually longer than that required for the initial impregnation step. However, when the deposits are present on acid resistant material, they may be equally well initially impregnated with a carbonate solution and then subjected to the action of an acid solution.

I claim as my invention:

1. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the interstices of said deposits containing an acid having a dissociation constant not less than approximately 10^{-5}, the step comprising subjecting said deposits to the action of an inorganic carbonate solution and thereby generating carbon dioxide gas within the interstices of said carbonaceous deposits.

2. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the interstices of said deposits containing an acid having a dissociation constant not less than approximately 10^{-5}, the step comprising subjecting said deposits to the action of an inorganic alkali carbonate solution and thereby generating carbon

dioxide gas within the interstices of said carbonaceous deposits.

3. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the interstices of said deposits containing an acid having a dissociation constant not less than approximately 10^{-5}, the step comprising subjecting said deposits to the action of a heated inorganic alkali carbonate solution and thereby generating carbon dioxide gas within the interstices of said carbonaceous deposits.

4. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the interstices of said deposits containing sulfuric acid, the step comprising subjecting said deposits to the action of a sodium acid carbonate solution and thereby generating carbon dioxide gas within the interstices of said carbonaceous deposits.

5. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the steps comprising impregnating the interstices of said deposits with an acid having a dissociation constant not less than approximately 10^{-5} and thereafter subjecting said acid impregnated deposits to the action of an inorganic carbonate solution whereby carbon dioxide gas is generated within the interstices of said carbonaceous deposits.

6. In a method for removing porous carbonaceous deposits resistant to the action of strong surfuric acid from surfaces to which they adhere, the steps comprising impregnating the interstices of said deposits with an acid having a dissociation constant not less than approximately 10^{-5} and thereafter subjecting said acid impregnated deposits to the action of an inorganic alkali carbonate solution whereby carbon dioxide gas is generated within the interstices of said carbonaceous deposits.

7. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the steps comprising impregnating the interstices of said deposits with sulfuric acid and thereafter subjecting said impregnated deposits to the action of an inorganic alkali carbonate solution whereby carbon dioxide gas is generated within the interstices of said carbonaceous deposits.

8. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the interstices of said deposits containing sulfuric acid, the step comprising subjecting said deposits

to the action of an aqueous solution containing approximately 5% by weight of sodium acid carbonate for a period of approximately 30 minutes at a temperature of approximately 100° C., whereby carbon dioxide gas is generated within the interstices of said carbonaceous deposits.

9. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the step comprising reacting within the interstices of said carbonaceous deposits an inorganic carbonate solution and an acid having a dissociation constant not less than approximately 10^{-5}, thereby generating carbon dioxide gas within said interstices.

10. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the step comprising reacting within the interstices of said carbonaceous deposits an inorganic alkali carbonate solution and an acid having a dissociation constant not less than approximately 10^{-5}, thereby generating carbon dioxide gas within said interstices.

11. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the step comprising reacting within the interstices of said carbonaceous deposits an inorganic alkali carbonate solution and sulfuric acid, thereby generating carbon dioxide gas within said interstices.

12. In a method for removing porous carbonaceous deposits resistant to the action of strong sulfuric acid from surfaces to which they adhere, the step comprising reacting sulfuric acid with sodium acid carbonate solution within the interstices of said carbonaceous deposits, thereby generating carbon dioxide gas within said interstices.

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