RECENT INDUSTRIAL APPLICATIONS OF ION EXCHANGE

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Many boiler and steam turbine operators are well acquainted with the problem of siliceous deposits on boilers, steam conduits, and turbines. Normally, it is taken for granted that maintenance alone is the solution in keeping these surfaces, lines and equipment clean for efficient performance. Unfortunately, there is no general formula which can be applied to correct the silica deposit phenomena. There have been many investigators in the field, perhaps the most widely known of these men is Professor Straub of the University of Illinois. He has indicated in various reports that silica deposits in high pressure steam systems have been detected when the steam silica concentrations become greater than 1/10th ppm. His work has suggested to operators that one means to inhibit silica deposits is to employ sodium and potassium chloride salts along with higher pH values in the boiler water. Some effectiveness has been noticed when this suggestion has been followed.

Mr. Walter Leaf, Research Technician for the Denver & Rio Grande R.R., has reported high silica adsorption values in hydrous ferric oxides. His work on low silica waters, however, indicate that he is unable to reduce the silica content to less than 1 ppm with this method. Other procedures such as the use of metal oxides and hydroxides are being used but again published reports for the most part show reduction in silica to 1 to 2 ppm, which is a range that still leaves heavy amounts of silica to concentrate in the boiler. It is the intent of this paper to present a method and to describe equipment now being put in service in the Southwest whose function it is to remove silica from an original concentration of 8.5 ppm SiO_2 to an effluent concentration not to exceed .2 ppm at flow rates of 300 gallons per minute. The water will be supplied at a pressure of 50# to 90# per square inch and at a maximum temperature of 90° F. The analysis of the water is as follows:

Figure I

Ca	12 ppm	Na	188 ppm
Mg	14 ppm	SO_4	146 ppm
HCO_3	103 ppm	SiO_2	8.5 ppm
CO_3	22 ppm	TSS	12.4 ppm
OH	0 ppm	TDS	613 ppm
Cl	164 ppm	NH_3	0.10 ppm
		pH	9.0 ppm

The water is to be passed through a cation and an anion unit placed in series. The cation exchanger employs a resin with replaceable hydrogen for the cations of the raw water and the anion material contains active amino groups which adsorb the resultant acid equivalent from the cation exchanger. The cation exchange resin is regenerated with acid and the anion resin with alkali.

This, of course, is a brief resume of the principle of De-ionization which has been discussed in detail at former meetings of this society.

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Figure II Cation & Anion Exchange Reactions:

$$CaSO_4 + 2HR \text{ ------------ } H_2SO_4 + Ca\,(R)_2$$

$$MgCl_2 + 2HR \text{ ------------ } 2HCl + Mg\,(R)_2$$

$$H_2SO_4 + RNH_2 \text{ ------------- } RNH_2 \cdot H_2SO_4$$

$$HCl + RNH_2 \text{ ------------ } RNH_2 \cdot HCl$$

Water freed of its mineral content by this process is not suitable for high pressure boiler work because of two outstanding limitations in the process. Carbonic acid is not effectively removed because of its low ionization constant nor is silica or silicic acid by the same token. Carbon dioxide, however, can be removed from the effluent by means of vacuum de-aeration and this method of CO_2 removal is being used on this installation.

Stoichiometric Titration curves of anion resin indicates that adsorption of carbon dioxide is effected on newly regenerated anion material through its basicity, but is soon exhausted for carbon dioxide adsorption. Silica and silicic acid being more weakly ionized than carbonic acid, show no tendency for adsorption all through the service cycle. It was observed and reported last year that anion exchange resins showed very definite adsorption values for silica when the highly ionizable fluosilicic acid values were tested. Accordingly, a new adaptation in the field then, and one to be employed on the installation referred to here, involves the conversion of silica and silicic acid to the highly ionizable fluosilicic acid H_2SiF_6. Fluosilicic acids ionization constant is greater than that of hydrochloric acid, hence, its adsorption is preferential to either hydrochloric, sulphuric or carbonic acid. The method which has been selected for silica removal in this installation, is that of feeding sodium fluoride to the cation exchanger at a point where the calcium and magnesium of the raw water has been exchanged. The point selected is determined by the percentage of calcium and magnesium in the total solids of the raw water. Furthermore, it is thought that at this point of injection the preponderance of acidity prevents the precipitation of calcium and magnesium fluoride. The initial reaction at the feed point of sodium fluoride follows:

$$R - H + NaF \text{ -------- } R - Na + HF$$

The hydrofluoric acid is then left free to react with silica for the conversion to fluosilicic acid. This resultant acid is adsorbed on the anion resin.

$$(6HF + SiO_2 \text{ ---- } H_2SiF_6 + H_2O)\ 2R - NH_2 + H_2SiF_6 \text{ ----- } (RNH_2)_2\ H_2SiF_6$$

Fluosilicic acid is a stable acid as long as pH values are kept lower than four. This, of course, complicates the normal regenerations of the anion exchanger; namely, that of regeneration with an alkali; an alkali regeneration would precipitate silica if normal procedures were followed. It is necessary, therefore, to deviate from standard procedure. To preclude the possibility of depositing insoluble silica, the anion bed is washed with the excess acid of the cation regenerant. There is a replacement reaction involved in the procedure which replaces and washes to the drain the fluosilicic acid of the anion exchanger with incoming acid of the cation exchanger. This procedure is then followed with a regeneration with an alkali as in the usual regenerating cycle.

$$2R - NH_2 \cdot HCl + NaOH \text{ ------ } 2RNH_2 + H_2O + NaCl$$

Investigation is being conducted to determine whether a strong salt will effectively remove fluosilicic acid as well as mineral acids or not. There has been some indication that sodium chloride effectively converts the adsorbed fluosilicic acid to its respective slat, converting the anion resin, in turn, to its hydrochloride form for later base regeneration.

To give us some conception of the scope of the work being undertaken for silica removal, the following slide will show the equipment involved. Raw water enters the cation exchanger through a conventional distributing system at the top, and is collected through a series of bottom distributors. In order to effect silica removal, there are two additional distributors necessary other than the conventional distributors discussed. One of the distributors is suspended immediately above the resin and it is used to introduce the regenerant, HCl, into the bed after it is exhausted. The second additional distributor is buried in the resin bed. It is through this distributor that the sodium fluoride is pumped during the service cycle.

It is of interest to note here the methods employed in both the cation and anion exchange tank to prevent clogging of the regenerant distributors during backwashing, and in the case of the cation tank to keep clear the sodium fluoride distributors buried in the resin bed. A system of Foxboro flow regulators bleeds off a small amount of raw water and inducts it through the caustic, acid and sodium fluoride distributors with sufficient head to prevent any resin entering the system.

The sodium fluoride is stored in a 4' x 6' steel tank from which the sodium fluoride is drawn through a 3/4" pipe and injected into the side of the tank through the buried distributors. The sodium fluoride is introduced throughout the entire service cycle of the Deionization process. The concentration, rate of flow, and depth at which the distributor is placed is determined by the percentage concentration of the calcium salts in the raw water as has been described. There is a momentary reaction in which the sodium fluoride thus introduced, is converted to hydrofluoric acid which then reacts with the silica to form fluosilicic acid and is passed as such to the anion exchanger along with the usual mineralacids of the cation exchanger.

Theoretically, at least, in the anion exchanger fluosilicic acid being a stronger acid than the other mineralacids, would indicate that adsorption of the fluosilicic acid would be effected at the top of the anion bed. It is for this reason, then, that the unique principle of backwashing with acid from the cation exchanger is done, so as to easily wash the fluosilicic acid quickly from the bed without fouling the resin, as might be the case if acid rinses were effected downflow. The mineral-free silica-free water, still heavily contaminated with carbon dioxide, is pumped to a 4' x 22' vacuum de-aerator. The vacuum will be produced by a three-stage steam jet ejector with sea water used for cooling the barometric condensers.

Of some interest to this audience should be the work conducted experimentally on sugar beet juices and molasses at the Layton Sugar Company, Layton

Utah. A pilot plant, built in triplicate, of suitable design was used for our study this year. Tank diameters and suitable bed depths were used to provide flow rates of 150 to 200 gallons of juice per hour.

The scope of the work undertaken this past campaign was threefold in purpose. The division of work included the (1) De-ionization of second carbonation juice (2) yard molasses, and (3) direct De-ionization of raw beet juice. It must be admitted that the emphasis of the work was directed during the campaign on second carbonation as it was felt that clear juices free of suspended matter and colloids and at low brix would provide the best medium for dissolved solid removal studies.

The juices were suitably cooled and passed through a double system of cation, anion exchange. Juices of high purity were obtained but regardless of the low temperature involved, it was noted that inversion percentages were too high to make the process practical. Accordingly, it was determined soon after studies began, that on the treated juices to hold inversion at absolute minimums it was necessary to employ the single stage of cation and anion exchange.

The second carbonation juice tested 91% purity. Following the exchange cycle this purity was increased to a 99% purity average. This high purity juice was then concentrated to 65 or 66 brix after which it was crystallized in a special vacuum pan built for the studies. Needless to say this high purity juice handles somewhat differently than normal juices in the vacuum pan but certain techniques were soon developed so that good crystallization was effected. The resultant sugar was pure having ash content of .001%. It was possible for us this year to segregate the high green from the first strikes. These high greens were concentrated and crystallized, giving white intermediate sugar, ash free. It was felt that if subsequent collections of greens were possible that additional white strikes could have been obtained.

By calculation it was determined that the yield increase through De-ionization would be approximately 29 pounds increase per ton of beets processed, keeping in mind that the sugar content of the beets being processed was 14.50% sugar.

Cost studies indicate that the amount of additional sugar salvaged vs. the cost of regenerating the units were highly satisfactory (82.5 pounds of sugar increase per $1.55 investment for regeneration).

The second phase of the work conducted centered around the treatment of yard molasses. This material was brought to the De-ionizers at 35 brix. It was determined that inasmuch as inversion would be acceptable at higher concentrations than in the raw products, that it would be best, because of the high mineral content, to double pass the yard molasses. Accordingly the material was passed through at high temperature. Temperatures for the most part did not exceeed 160° F. The resultant effluent was sent to the evaporators and concentrated to 65 brix. The inversion at this temperature naturally enough, was high, and percentage-wise fell in the range of 5 to 13%. The material, however, was free of turbid and suspended matter and was found to be suitable for human consumption. The ash content was approximately .3%.

This edible material is of such purity and sweetness that it was felt that it could aid in the program of the sugar manufacturer in providing not only the housewife but the industrial customer as well, with the necessary sweetness so sorely needed during these days of sugar rationing. This in substance then, is a means of providing for human use a substance once looked upon by the sugar man as a by-product of little value, except as a stock food.

It was soon determined that this process would not have been successful had the investigators not been able to work at elevated temperatures in the backwash cycle as well as in the actual regenerating cycle as it was the only means of removing accumulated gums and colloidal matter adsorbed during the service cycle on the exchange media.*

Toward the end of the sugar campaign it was felt that capacity data, stability studies and general information had progressed to the point where the third phase of the work could be investigated. The attempt at this point was to eliminate liming as it is normally carried out in a sugar factory as well as the carbonation and sulphitation steps and first filtration. At the outset the attempt of the researchers was to eliminate all filtration, however, as the work progressed it was soon decided that perhaps one filtration step may be needed in subsequent studies of this kind. In general it can be said that the raw juice at suitable temperatures and with only a fraction of the lime normally used for flocculation is allowed to pass to the De-ionizers under pressure at low brix. The juice at this point is heavily contaminated with the colloids and mineral matter so familiar to the sugarman; however, its purity is 84%.

It was observed that the incoming juice so treated could be filtered almost satisfactorily in the De-ionizing step. A water-white effluent was collected and analyzed. The purity of the juice following De-ionization by this method was observed to be 98.5 to 99%. The juice so obtained was concentrated and crystallized with first and second strikes being white ash-free sugars. The costs, of course, would be comparable to those costs reported in second carbonation treatment, however, one must consider that in the process liming, carbonation, sulphiting expenses are removed. It is not to be construed that the work on raw beet juice is conclusive. Some difficulties were observed in the process that indicated that a filtration step might be required. These filters would necessarily have to be of special construction so as to eliminate tendency of corrosion on the filter plate by a highly acidified sugar juice.

Facilities and time being factors during the experiment did not allow for investigation along these lines, however, the indication and conclusion on raw beet juice is that it can be suitably De-ionized without liming, carbonation or sulphitation, the end product of which is a white, ash-free sugar.

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* Patents for this process have been applied for by the Illinois Water Treatment Company.