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FB-LINE RESIN TESTING FINAL REPORT (U)

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WSRC-TR-92-22

Page 1 of 8

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Derivative Classifier

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FB-LINE RESIN TESTING FINAL REPORT (U)

Summary

The Dowex 50W-X8 and 50W-X12 resin samples are both strong acid cation materials in the hydrogen form. Each material has a water retention capacity characteristic of its respective marketed degree of cross-linking. Dowex 21K gives confirmatory responses to tests for a strong anion exchange resin in the nitrate form. All three resins have the manufacturer's specified ionic type and form, and the Dowex 50W resins have characteristic water retention capacities. These tests conclude that the ion exchange resins in use in FB-Line meet the approved safety document criteria for cross-linking, ionic form, and resin type.

Introduction

In late November a request was received from J. B. Schaade of Separations for verification of a cation exchange resin's (Dowex 50W-X8) compliance with the approved OSR and Technical Standards in connection with FB-Line restart. This request was expanded in mid-December to include an additional cation resin, Dowex 50W-X12, as well as an anion resin, Dowex 21K. Since the resin supplier, Dow Chemical, U.S.A., is not an SRS QA approved vendor, the site can no longer rely on their QA program to confirm compliance with the OSR (DPW-85-101 Rev. 1) and Technical Standards (DPSTS-221) as has been the past practice.

Verification needed to establish the type of exchange sites on each resin, strong acid in the case of the two cation materials and strong base for the anion resin. It was also necessary to establish the ionic form of each resin. The cation resins were to be in the hydrogen form while the anion resin was to be in the nitrate form. Additionally, a cross-linkage requirement of 8-12 % had to be met by each of the cation exchange resins.

Typically, the verification of each new resin shipment has been accomplished by the use of the vendor QA program and testing performed by the Essential Materials Lab. The

additional testing performed in SRL will be utilized to develop new analyses for use in the Essential Materials Lab which will replace the reliance upon the vendor QA program. In addition, these tests will confirm the compliance of the current resin with the OSR and Technical Standard requirements.

Experimental

In order for the Essential Materials Laboratory to develop procedures for testing future resin samples for compliance with the established guidelines, a set of the testing procedures employed here has been issued (SRL-ATS-91-0325). This section will contain only a summary of the testing procedures specified in detail in the aforementioned ATS document.

Materials

Resin materials tested included Dowex 50W-X8 (Lot No. MM910314-F), Dowex 50W-X12 (Lot No. MM860630-F), and Dowex 21K (Batch No. 12701). Reagent grade hydrochloric acid (J. T. Baker), sodium nitrate (Mallinckrodt), sodium sulfate (Mallinckrodt), and silver nitrate (J. T. Baker) were utilized. All solutions were made with deionized water.

Testing Procedures Summary^{1,2}

The ionic type and form of the two cation exchange materials were checked in triplicate by two procedures. In Test I a set of samples was equilibrated with deionized water for one hour prior to decanting and rinsing with additional deionized water until the supernatant pH was greater than 5. The resin sample was then equilibrated with a solution of 10 wt% NaNO_3 for an additional hour. The pH of the resulting supernatant liquid was measured with a pH meter. For Test II, an additional set of resin samples was equilibrated overnight (8 hours) in a 10 wt% HCl solution to insure conversion to the acid form. The acid solution was then decanted and the resin rinsed with deionized water, reequilibrated with a 10 wt% NaNO_3 solution, and the pH measured. Supernatant from these samples was also tested with AgNO_3 for the formation of a AgCl precipitate.

Samples of the anion resin were treated as described in Test II to verify the ionic type. To confirm the nitrate form of the anion resin (Test III), three samples were equilibrated with a solution of 10 wt% Na_2SO_4 for one hour prior to submission of the supernatant and initial Na_2SO_4 solutions, as a blank, to the Analytical Development Section for ion chromatography analysis.

Water retention capacity measurements were performed in duplicate on each of the Dowex 50W materials in their acid form by first equilibrating the resin sample with deionized water and then transferring the sample to a preweighed (T) centrifuge tube insert (Attachment A). After spinning the sample to extract the dead volume water, the insert and resin were

weighed (A), dried overnight (8 hours) at $107 \pm 3^\circ\text{C}$ and weighed (B) a final time. The water retention capacity was then calculated from the following equation:

$$\% \text{ water retention} = [(A-T) - (B-T)] \times 100 / (A-T)$$

Results

Test I:

<u>Sample No.</u>	<u>pH</u>
50WX8-1	≤ 0.9
50WX8-2	≤ 0.9
50WX8-3	≤ 0.9
50WX12-1	≤ 0.8
50WX12-2	≤ 0.8
50WX12-3	≤ 0.8

Test II:

<u>Sample No.</u>	<u>pH</u>	<u>AgCl ppt</u>
50WX8-1	≤ 0.9	trace
50WX8-2	≤ 0.9	none
50WX8-3	≤ 0.9	none
50WX12-1	≤ 0.9	none
50WX12-2	≤ 0.8	none
50WX12-3	≤ 0.8	none
21K-1	4.6	copious
21K-2	4.6	copious
21K-3	4.7	copious

Test III:

<u>Sample No.</u>	<u>ADS Sample No.</u>	<u>[NO₃⁻], mg/L</u>	<u>[SO₄²⁻], mg/L</u>
21K-1	2-68927	6697	65824
21K-2	2-68928	6491	66016
21K-3	2-68929	6826	68151
blank	2-68930	<100	75594

Water Retention Capacity:

<u>Sample No.</u>	<u>% water retention</u>
50WX8-1	55.2
50WX8-2	54.1
50WX12-1	47.9
50WX12-2	48.4

Discussion

A strong cation resin in the acid form will release protons when equilibrated with a solution of sodium ions due to the higher selectivity of the resin for sodium and other metal ions. A weak cation resin will not display the same degree of affinity for sodium ions and hence the resulting supernatant liquid following equilibration will be much less acidic because the pH will be buffered by the weak acid (generally carboxylate groups on the resin). The sulfonate groups on Dowex 50W resins are highly acidic and will not buffer the supernatant liquid when converted to the sodium form, hence the supernatant liquid will have a pH well below 2; the exact value is dependent on the amount of resin converted. Additionally, if a cation resin is equilibrated with a solution of hydrochloric acid and rinsed thoroughly, it can readily be distinguished from an anionic resin following a second equilibration with a solution of sodium nitrate through a simple qualitative test for chloride ions. Equilibration with hydrochloric acid will create a chloride complex of an anionic resin. Chloride ions will be displaced when the resin is reequilibrated with the sodium nitrate solution, and addition of silver nitrate to the supernatant will result in formation of an insoluble silver chloride precipitate. Only a trace of precipitate will result if the resin is a weak anion material, whereas considerable precipitate will be present if the resin is a strong anionic resin due to the fact that the chloride ions present in solution will not be buffered by the resin. In the case of a strong or weak cation resin, no precipitate of silver chloride will be present because no chloride complex will have been formed during the equilibration with hydrochloric acid.

The results indicate that both the Dowex 50W-X12 resin currently in place in FB-Line and the Dowex 50W-X8 resin which will replace it are strong acid cation resins in the hydrogen form. All samples tested had pH's below 1 and, with one exception, gave negative tests for complexation of chloride ions. The one sample in Test II (50WX8-1) which showed a hint of silver chloride precipitate was a result of insufficient rinsing of the resin after equilibration with hydrochloric acid prior to reequilibration with the sodium nitrate solution.

The Dowex 21K resin is a strong base anion resin. The pH of the supernatant liquid following equilibration with sodium nitrate was a little lower than predicted for a strong base resin but greater than that predicted for a weak anion material.² This can be explained

by the fact that the anticipated neutral solution would be unbuffered and hence strongly influenced by the degree to which the resin was rinsed following the equilibration with hydrochloric acid. A copious precipitate of silver chloride resulted when the supernatant liquid was tested following equilibration of the material with a solution of sodium nitrate, further confirming the strong base nature of the resin.

Ion chromatography indicated the release of nitrate ions from the Dowex 21K resin when equilibrated with a solution of sodium sulfate. While the amount of nitrate ions released is greater than that predicted due to the decrease in the corresponding concentration of sulfate ions from the blank, the fact that the two measurements were made on different scales reasonable explains the discrepancy. If some of the resin were in an ionic form other than nitrate, the amount of nitrate ion released would have been less than expected, and this is not observed.

While a specific test for cross-linking is not available, discussions with Dow Chemical, U.S.A.³ have indicated the Dowex 50W resins have not changed in formulation since their introduction and hence the water retention capacity test is an appropriate indicator of the nominal degree of cross-linking within the resin. However, newer resin formulations than the Dowex 50W materials do not have water retention capacities characteristic of their degree of cross-linking because of the methodologies employed in their formulation. Dow has provided manufacturing specifications for the water retention capacity of Dowex 50W-X8⁴ (Attachment B) but no longer have available the specifications for their discontinued Dowex 50W-X12 resin.³ Additionally, all samples of Dowex 50W-X12 which were employed in the original establishment of the Technical Standard specifications and earlier measurements of resin characteristics have been disposed and hence are unavailable as reference materials.⁵ A literature value has been utilized as an independent measure of the water retention capacity one would expect for this material.⁶

The two samples of Dowex 50W-X8 resin tested had water retention capacities in the acid form of 55% and 54%, respectively. Dow Chemical's manufacturing specification for this material is 50-56% (Attachment B) and the literature value is 53%.⁶ Both Dow and the literature value cited are for a drying method as utilized in this work. In the case of Dowex 50W-X12, both resin samples tested have a water retention capacity of 48%. The literature specified value is 46%.⁶ If the resin were greater than 12% cross-linked, one would expect a water retention value considerably less than 46% because the extra cross-linking would reduce the water retention capacity. Since the Dowex 50W-X12 water retention capacity indicates a cross-linking slightly less than 12%, this confirms that the resin is within the Technical Standard limits.

Recommendations

In light of the current understanding that there is no direct measure of cross-linking for new

resin materials because of the current methods of formulation, it would be advisable to revise the Technical Standards to reflect the specific properties of the resin material which are actually of interest (ie. swelling, water retention capacity, etc). It appears that in the past too much emphasis has been placed on the manufacturer's stated cross-linking, rather than the factors which make one resin acceptable to the process and another one unacceptable. With the discontinuation of Dowex 50W-X12, one must consider if Dowex 50W-X8 will continue to be available indefinitely. A substitute resin with the same water retention capacity and swelling characteristics may be acceptable but the current Technical Standards do not reflect this.

References

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Attachment A - Glass Centrifuge Tube Insert

Attachment B

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Metal Recovery product data

DOWEX* 50WX8 50/100

MATRIX STRUCTURE	MICROPOROUS STYRENE/DVB
TYPE	STRONG ACID
PHYSICAL FORM	HARD, OFF WHITE TO LIGHT BROWN COLORED, SPHERICAL BEADS
IONIC FORM	HYDROGEN
TOTAL EXCHANGE CAPACITY	1.7 MEQ/ML MINIMUM
WATER RETENTION CAPACITY	50-56%
PARTICLE SIZE	15% MAXIMUM + 35 MESH 15% MAXIMUM - 80 MESH

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