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Executive Summary

Alkaline solutions soaking are the most accepted treatment for the desalination of archaeological iron in an attempt to arrest further detrimental corrosion. The process displaces chloride ions (desalination) and diffuses them out of the artifact. The method relies on high concentrations of hydroxide and low concentrations of chloride in the solution. As the treatment progresses, chloride concentration increases decreasing desalination rates and the technique's effectiveness. Conservators cope with this issue by regularly replacing solutions. This procedure generates significant quantities of waste, and requires personnel and considerable amounts of water and sodium hydroxide. The proposal aimed at investigating the applicability of ion-exchange technology to remove chloride from solution without the need to constantly replace the soaking solutions.

Depending on the volume, mass, shape, composition and condition of the artifacts, hundreds if not thousands of gallons of NaOH solution may be required to optimize and maintain the chloride concentration gradient between the artifact and the treatment solution. It is believed that where an ion-exchange resin is employed, the recirculating solution ensures a constant pH and a maximum chloride release, resulting in a decrease in overall treatment times. The recycle-ability introduced by the utilization of a resin would allow for an unprecedented development opportunity for stabilization treatments. A single volume of solution would be continuously recirculated through the resin bed, allowing for considerable reduction in the amount of treatment solution produced and subsequently disposed of, therefore drastically reducing labor, cost and health and safety issues. These benefits would also be applicable to the subcritical treatment resulting in significant up-scaling of the technique. Reductions in volume of solution needed would possibly allow larger artifacts, such as cannon to be treated. Due to their regeneration capability (life-cycle of 5-10 years), ion-exchange systems provide an environmentally friendly, cost-effective and sustainable treatment option for the desalination of metallic cultural heritage.

Introduction

All over the world large quantities of archaeological iron (weapons, tools, architectural elements) have survived into modern times. On excavation, these objects exhibit a wide range of preservation states, and have been exposed to a combination of mechanical and/or chemical damage. Following recovery, chemical damage - and corrosion in particular - presents a significant threat, as materials are often removed from environments in which they had previously reached equilibrium.

Especially for artifacts recovered from underwater sites, interventive stabilization treatments commonly entail the removal of chloride (and other salts) from the metal and corrosion layers. Failure to reduce the chloride concentration to minimum levels, may translate into the loss of the information contained on the original surface of the artifact and the artifact itself.[1-6]

Regardless of the desalination treatment employed - simple soaking, cathodic polarization, subcritical - iron stabilization is carried out in alkaline solutions, which provide hydroxide ions (OH^-) to replace chloride ions (Cl^-). In all these treatments, the solution carrying the OH^- must reach the sites where the Cl^- are located and the exchange occurs, which often means penetrating through pores and interstices following paths with high degrees of tortuosity.[7-9] The newly released chloride ions must diffuse out through the material towards the bulk of the treatment solution. The driving force of the chloride diffusion is the concentration gradient between the artifact and the bulk of the treatment solution. The concentration gradient can be maximized by keeping the amounts of chloride in solution at negligible levels.

Conservation treatment protocols continuously require re-evaluation so that best-practice techniques reflect contemporary scientific capabilities. As such, frequent meshing of the conservator's skills with those of the materials science and chemistry profession is imperative. The *primary objective* of this project was to design and implement an improved treatment protocol, that is effective, fast, reversible, sustainable, safe, and in accordance with conservation ethics.

We proposed to apply ion-exchange systems to separate chloride salts from alkaline solutions traditionally used to stabilize archaeological metal. A recirculating and regenerating system could be devised, which would accelerate the treatment of iron artifacts and use significantly less alkaline solution, therefore reducing handling and health and safety issues to a minimum.

Ion-exchange processes are reversible interchanges of ions between a solid and a liquid phase where the structure of the solid (cross-linked polymer resin) is not permanently altered. Ion-exchange resins are used in a wide range of chemical processing applications.[10-15] Major strengths behind the widespread use

of cross-linked polymers are: ease of processing and handling; simplification of separation and/or purification; and recovery and recycling of the supports for reuse.[16] Ion-exchange resins contain ion-active sites throughout their structure with a uniform distribution of activity. Depending on the type of ionic separation sought, several sub-categories of resins can be used. A cation-exchange resin is a negatively charged matrix capable of exchanging cations or splitting neutral salts across the entire pH range. They can either be weak or strong acid resins depending on the type of acid functionality introduced in the polymer matrix. In contrast, anion-exchange resins are positively charged capable of exchanging anions. They are typically obtained by introducing an amine functionality in the polymer matrix. Since ion-exchange resins are solid, insoluble (but reactive) acids, bases or salts, they are excellent candidates to replace traditional separation techniques.

Separation of salts can also be performed using a resin which contains both fixed cationic- and anionic-exchange groups within the resin structure allowing for the sorption of ion pairs (or salts) from a solution. These are known as amphoteric resins or ion-retardation resins.

Amphoteric resins have been incorporated in processes designed for the pulp and paper and the salt production industries.[17-20] High levels of chloride in the recovery cycle of kraft pulp mills has been reported to cause serious problems in the recovery boiler operation in addition to the formation of a corrosive environment. In salt production, ion-exchange resins are successfully used to purify brine. Both industries produce inexpensive commodities limited by economics, where high energy and the use of large amounts of solutions and chemicals are sometimes difficult to justify. An added advantage to these resins is the ease of regeneration by a simple water rinse, at which time the salt impurities can be recuperated and the resin reused.[21] Polymer recyclability and liquid phase recovery make the process cost-effective in the long term.

Devising a system to remove salts from treatment solutions would be significantly beneficial to traditional techniques used by conservators, and in particular to the emerging novel subcritical treatment. Among the advantages of this latter technique are: high efficacy in the removal of salts over a period of time that is significantly shorter than alternatives currently available to conservators; successful transformation of iron corrosion products into more thermodynamically stable phases; and proven long-term stability of specimens treated with this technology.[22-29] The recently developed 40L treatment reactor has been used to successfully perform mass-treatments of artifacts and materials from the *H.L. Hunley* submarine and archaeological iron tools from the National Park Service.[30] Even though the amounts of treatment solution used during the subcritical treatment are comparable with those for soaking or cathodic polarization, they are used within a few days period instead of spread in several months or years.

Incorporation of an ion-exchange capability into the subcritical process will provide a further improvement by reducing the quantity of solution required to complete the treatment. Indeed, large quantities of solution have been a considerable limiting factor in the development of the technique. This will open doors to further unprecedented scale up opportunities where large artifacts such as cannons could be treated.

During this proposed research the alkaline solution treatment will be tested in a flow-through column operation. The polymer resin will be placed in a chromatographic column. Diameter and length of the column will be adjusted to account for potential swelling of the resin and will allow periodic backwashes and maintenance of uniform air-free resin beds. Flow will be controlled by a recirculation pump, and the process efficiency will be evaluated by periodic sample collection and analysis.

Methods and Materials

Glass Chromatographic column set-up:

The resin bed was prepared by taking 400mL of dry resin, Dowex Retardion 11A8, obtained from The Dow Chemical Company and soaking it in deionized (DI) water for 4.5 hours. This was to test for any volume expansion when the resin is fully saturated. No expansion was observed.

The prepared resin medium was carefully poured in a glass chromatographic column (74cm length x 2cm diameter). The column was filled to a height of 70cm to avoid overflow, which yielded a bed of 70cm x 2cm which corresponded to a volume of 220cm^3. The resin column set-up is displayed in Figure 1 along with the prepared NaOH/NaCl solution.

Figure 1: Assembled column and solution

There were three main pieces to this column: 1) the glass column itself, open at both ends 2) the release nozzle made up of one glass attachment piece, a O-ring plus one plastic inner valve piece and 3) the main attachment piece securing the release valve to the column. This last piece was made up of four smaller plastic pieces used in conjunction to make a removable connector. The column was assembled with a glass wool insert to retain the resin. The column was then filled with 220mL of prepared resin.

Then, the NaOH/NaCl solution for the test cycle was prepared (solution 1). NaOH was purchased from Macron, ACS as pellets (assay>98.7%) while NaCl was obtained from BDH, USP (assay: 99.0-100%). The reported aqueous solution was 1.96M NaOH and 1.99M NaCl.[33] For a liter solution, 78.6g of NaOH and 144.4g of NaCl were mixed in DI water.

Following the reported procedure and prior to running the separation experiment, the resin bed needed to go through a pre-rinsing stage in order to perform at full capacity. This is so that the resin can reach equilibrium. The different solution cycles through the column were performed using a peristaltic mini-pump variable flow manufactured by Fisher Scientific. The pre-rinse cycle consisted of 5 bed-volumes of the prepared solution. The 2 liters pre-rinse solution was prepared in a separate large Erlenmeyer and labeled accordingly. After the five bed-volumes (1.1L) of the pre-rinse solution cycled through the column, a pre-rinse wash cycle of several bed-volumes of heated DI water was cycled through. The DI water pre-rinse wash cycle was heated to 80°C on a stirring/hot plate. The temperature through the column remained constant at 80°C by using a heating tape, connected to a thermocouple, wrapped around the column and connected to a temperature controller. Once the pre-rinse cycle was performed, the resin bed was ready for the separation experiment. The test cycle consisted of 25 mL of solution 1 ran through the column at a flow rate of about 6.4mL per minute as reported in the literature. Samples were taken every two minutes during the test run. Prior to the run, a pH-meter (Orion) was calibrated and sample vials were labeled and ready for use. Aliquots were neutralized and conditioned with nitric acid (HNO_3) and chloride ion levels were quantified by means of Quantabs® strips.

<u>Pre-rinse phase:</u>

During the pre-rinse phase of the experiment, it was noticed that the resin almost immediately changed color from a light sandy color to a dark tan color as shown in Figure 2. This occurred gradually from the top of the column down until the entire column was a dark tan. During this phase the pH was monitored and rose from about 8 to over 12.5. The average flow rate was calculated to 10.42mL/min.

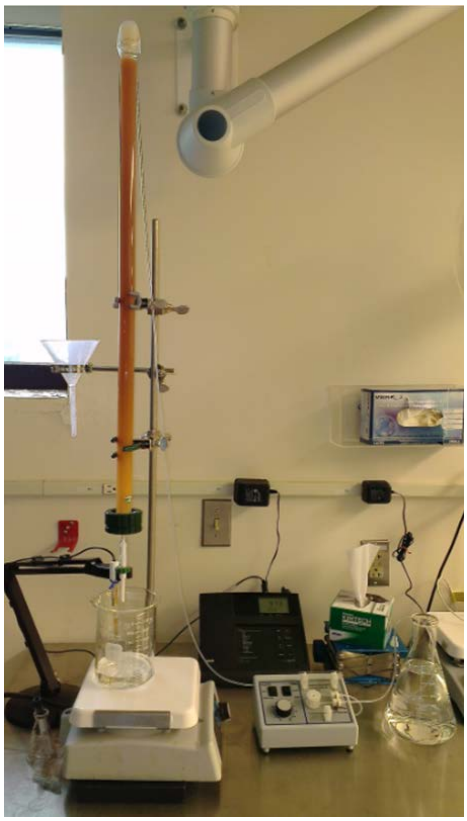

Figure 2: Full set-up.

Pre-rinse wash cycle

About 1.1L of DI water was placed in an Erlenmeyer, the water temperature was kept at 80°C using a hot plate, and pumped through the column wrapped with the heating tape. After about 30 minutes of this run the pH was measured to be about 12.7. The average flow rate for the pre-rinse wash cycle was 13.75mL/min. During this cycle it was noticed that few dry spots in the resin column appeared remained throughout the cycle. Figure 3 shows the biggest dry spot that was formed close to the top of the resin column. The wrapping pattern of the heating tape, initially chosen to enable monitoring of the resin, may be the reason for the dry spots, as heating may not have been consistent throughout the resin bed.

The flow rate during this cycle was particularly difficult to maintain as well as the liquid level above the column. Constant monitoring of the liquid level was required during this cycle. Figure 4 shows the setup of this wash cycle.

Typical separation experiment

A 250mL collection beaker was placed under the release nozzle of the column. 25mL of DI water was placed in the collection beaker so that the pH could be measured as soon as the liquid started eluting. Then, 25mL of the solution 1 to undergo separation was run through the resin bed.

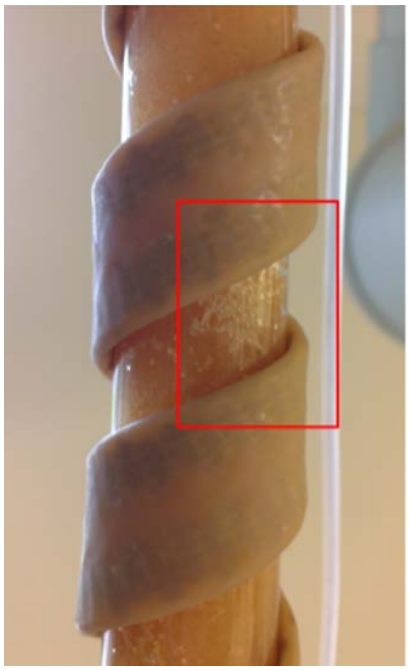

Figure 3: Dry Spots through the resin

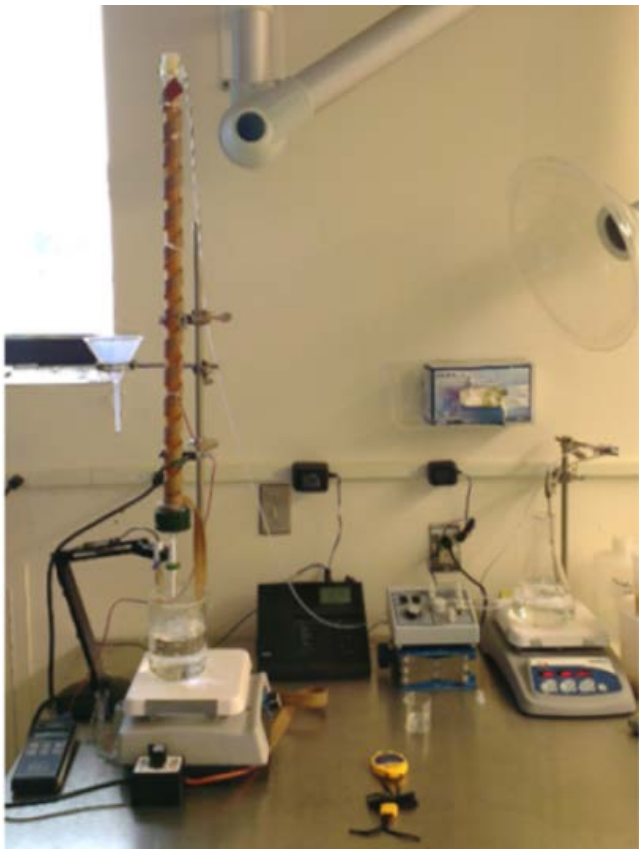

Figure 4: Pre-rinse wash cycle set-up.

Stainless steel column set-up

The column was built using stainless steel 316L tubing with a total length of 170cm, outer diameter of 1.9cm (O.D. 3/4in), and 0.124cm wall thickness (0.049in); able to hold about 366cm^3 of resin. The resulting final ratio length/width was about 100:1. At each end of the column 0.635cm (1/4in) ball valves were installed. All the fittings and valves were SS 316 (Swagelok). The new set up is shown in Figure 5. The eluent was driven through the column using a diaphragm digital dosing pump (Grunfos, Smart Digital DDC). This high precision pump allows flows up to 15L/h (4 gph) with a 1000:1 turn-down ratio. A silicone band heater was added to warm up the column and a type T thermocouple to measure the working temperature.

The system was mounted on a metal frame to facilitate its operation. All the containers used for the preparation, feed, and collection of the eluent were either polypropylene or Pyrex.

Figure 5: Stainless steel column set-up.

Results and Discussion

Determination of the resin suitability and capacity to retain chloride ions:

Several ion exchange resins from The Dow Chemical Company were initially identified and investigated for their suitability to selectively retain chloride ions from a caustic solution at room temperature and in a pH range from 10 to 14. [31] Fairly quickly into this investigation, it was realized that only few resins were suitable for effective separation of chloride ions and that even fewer would work in a high pH range.

A relatively new type of resin used in various separation processes, called Dowex Retardion 11A8, was selected for further investigation. Figure 6 shows the homogeneity in size of the resin. This resin is amphoteric containing both anionic and cationic adsorption sites which allow for the retardation of ions while they flow through its polymeric matrix in a chromatographic column. The resin is described in the literature as particularly useful in the purification of caustic soda (NaOH). [32-34] The two types of adsorption sites built-in the Dowex 11A8 resin are closely associated with each other, however, they have a selective attraction for mobile ions and can associate with them depending on the solution parameters, more specifically pH. Consequently, the resin can adsorb both anions and cations from solutions passing through the resin bed. The adsorbed ions can be easily displaced from the resin by simple wash with hot water as the eluant.

Incorporation of the resin into an exchange system:

Initially, the swelling behavior of the Dowex 11A8 resin was evaluated in a graduated cylinder in different conditions in order to plan further studies in a chromatographic column setting. The conditions examined were at room temperature and elevated temperature, in dionized water and in caustic solutions. No significant expansion of the resin was noticed in all conditions tested.

An important milestone in the testing of Dowex Retardion 11A8 was to reproduce results reported in the literature by the Dow Chemical Company referenced in this report. [33] Specifically, trying to duplicate the experiment for the separation of sodium hydroxide (NaOH) and sodium chloride (NaCl). The particular results to reproduce are shown in Figure 7, which is an excerpt of the document mentioned.

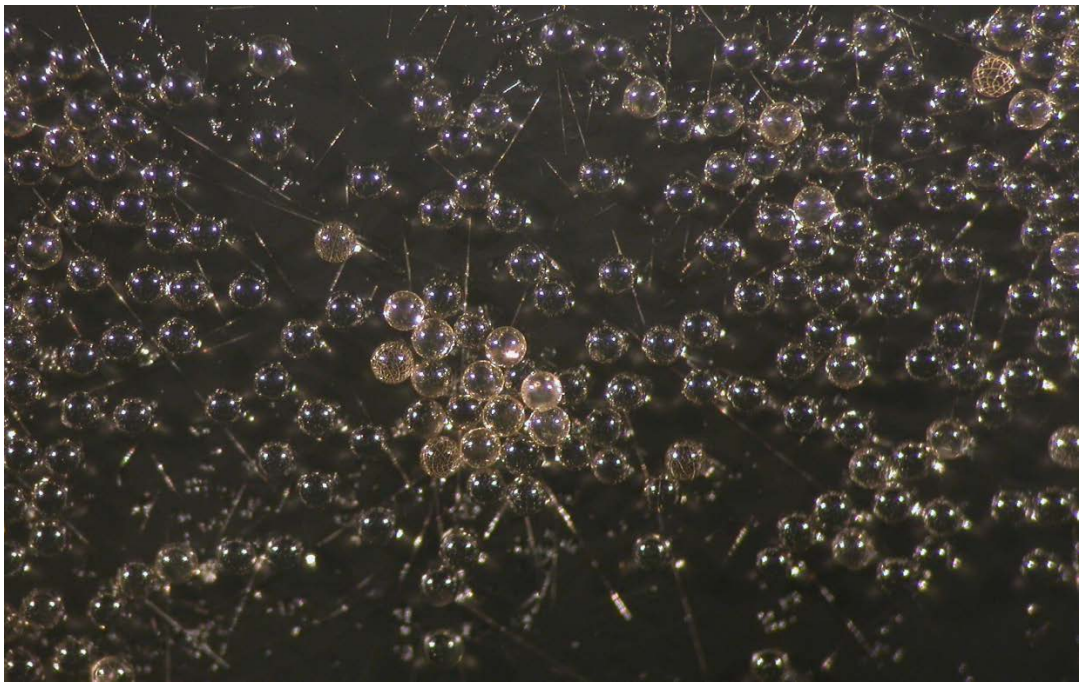

Figure 6: Dowex Retardion 11A8 micrograph

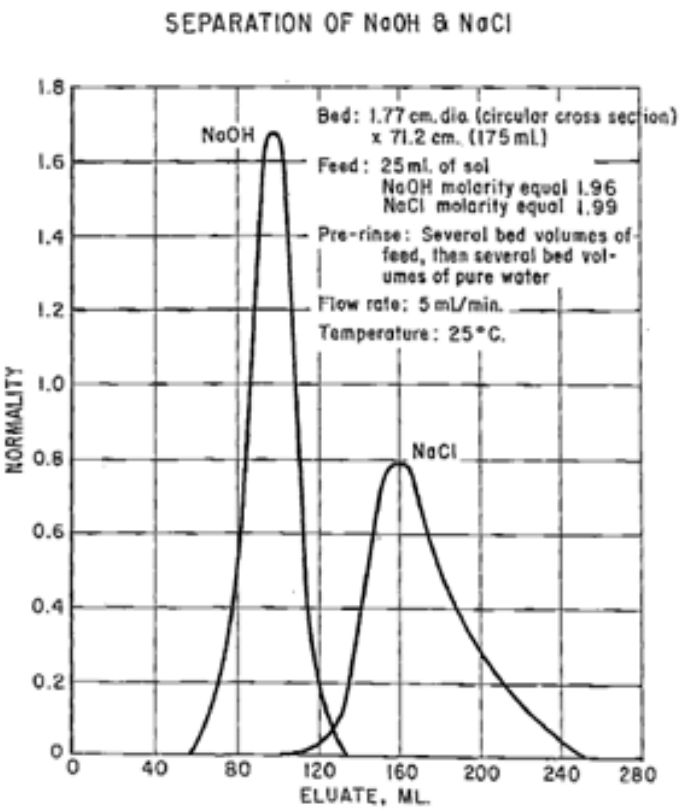

Figure 7: Dow results on NaOH and NaCl separation.[33]

Results of the first set of experiments are shown in Table 1.

		pH		Sample Size (grams)			
Sample	Time (min)	Collection Beaker	Sample	Before Dilution	After Dilution	Dilution Factor	Cl^- (ppm)
1	0:25	10.60	11.93	4.797	5.321	1.109	0
2	3:20	10.87	11.81	4.181	4.390	1.050	50
3	5:20	10.94	11.55	2.892	3.191	1.103	0
4	8:00	10.98	11.59	2.549	2.684	1.053	0
5	12:00	11.01	11.25	3.343	3.795	1.135	0
6	14:07	11.31	13.27	2.682	2.865	1.068	0
7	16:20	12.01	13.70	4.805	5.295	1.102	0
8	18:20	12.36	13.94	5.66	6.373	1.126	0
9	21:30	12.70	13.54	4.967	5.317	1.070	778
10	25:25	11.67	12.04	5.351	5.704	1.066	5775
11	28:40	11.46	11.76	5.436	5.744	1.057	6921
12	32:30	11.35	11.73	6.512	6.771	1.040	6966
13	36:34	11.33	11.40	4.819	4.848	1.006	5451

Table 1: Example of separation results through a glass column.

The data obtained show good separation of NaOH and NaCl in the samples collected. After converting the data to molarities, Figure 8 was constructed to directly compare the results obtained to the ones reported by The Dow Chemical Company.[33] It can be observed that good separation was achieved but the concentrations of both NaOH and NaCl was less than optimal.

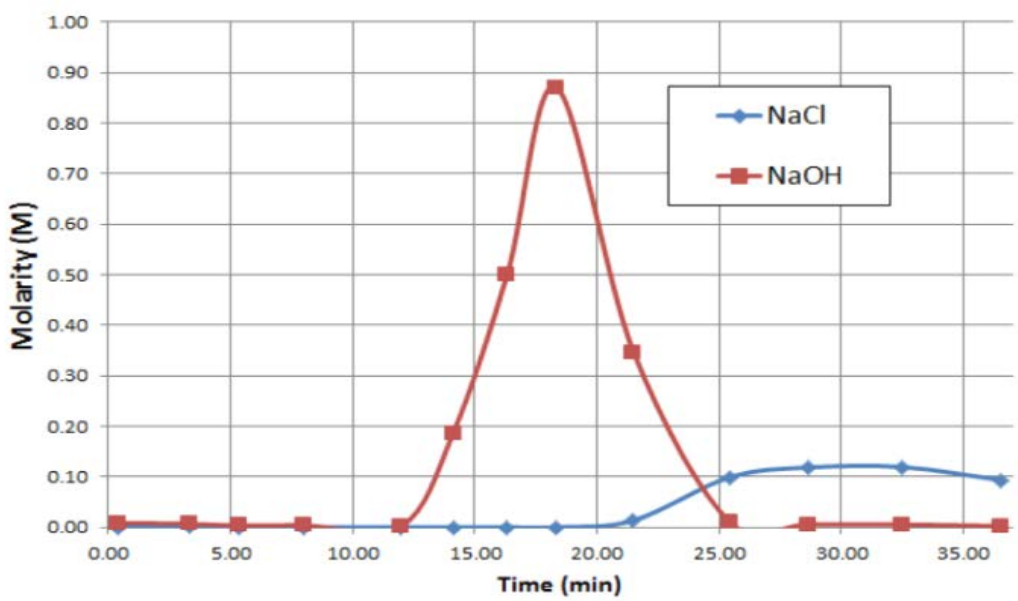

Figure 8: Experimental results in Molarity.

Another set of experiments was designed where the sampling was increased from 13 to 60 aliquots in order to better resolve the result readings. The eluate represented 360mL with a flow rate of about 5.81mL/min. The column set up is shown in Figure 9, and the results are presented in the Figure 10.

Much less equipment was used in this run as the same column bed was used which did not need to be equilibrated with hot DI water. Figure 10 shows a well defined separation and a slight improvement of the concentration, however, levels described by the Dow Chemical Company are not achieved.[33]

Figure 9: Separation experiment with a larger set of samples (60).

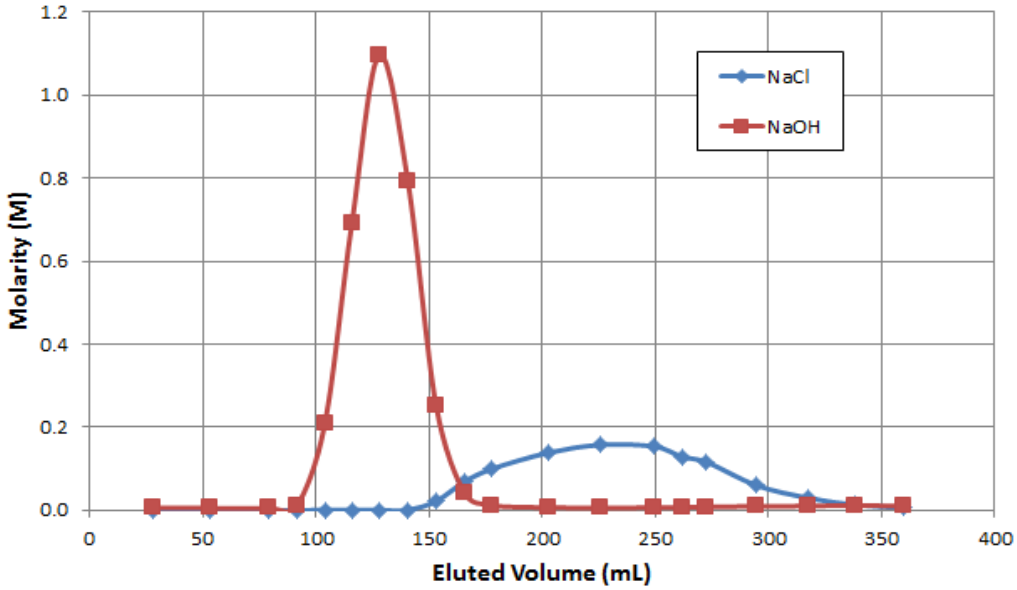

Figure 10: Separation experiment with an eluate of 360mL.

In order to eventually incorporate such a resin system in a artifact desalination process, it was important to determine if the resin could separate a NaOH and NaCl solution in iterations.

Test runs of 25mL of solution 1 followed by 100mL of DI water and a final water flush were performed. The results are shown in Figure 10 where the average flow rate was calculated to be 6mL/min.

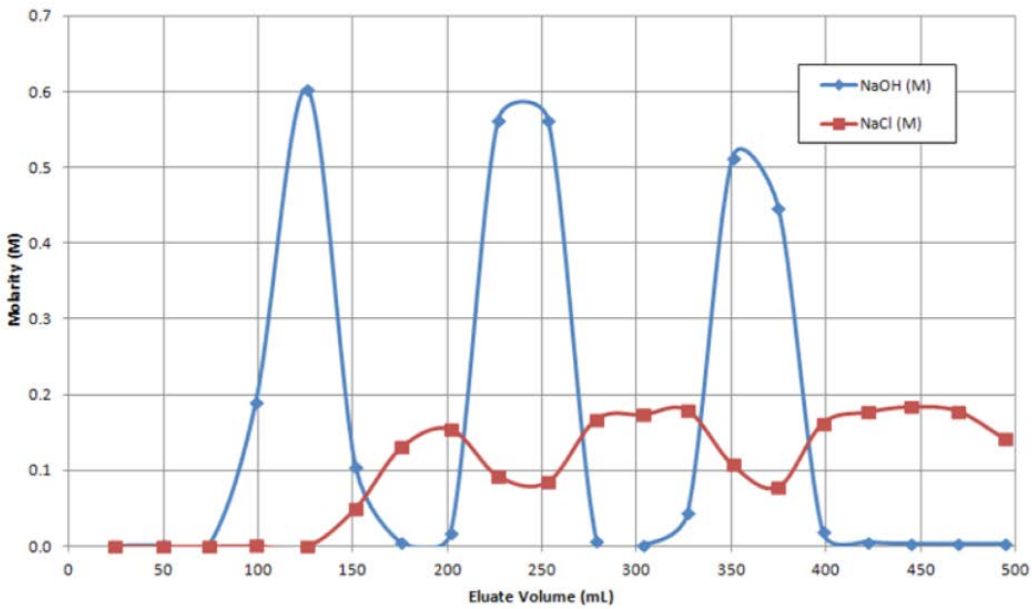

Figure 11: Separation experiments in iteration.

The results showed in Figure 11 confirm that the set-up and resin type will separate the solution into its two components in iterations. The NaCl could probably be better separated from NaOH with few modifications such as a longer column or additional amount of DI water in between test solutions.

This was implemented by building a new set-up out of stainless steel tubing which would allow an increase in the ratio column length/column diameter. For the experiments ran in the stainless steel column 25mL of a newly prepared 2M NaOH, 2M NaCl solution were used. The column was pre-rinsed with 2 liters of the same solution followed by 2 liters of DI water. The average flow rate was 6.67mL/min.

A longer column, and therefore resin bed, should implied more efficient and better separation between NaOH and NaCl. However, after the first series of runs, results looked more overlapped than with the initial shorter glass column, as shown in Figure 12.

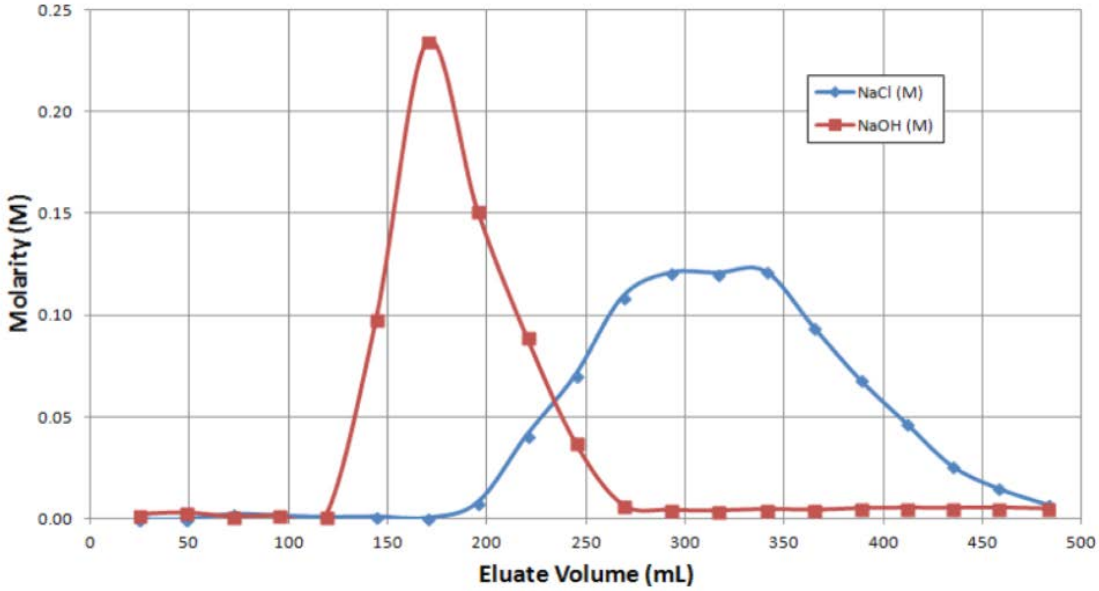

Figure 12: Set of results obtained with the stainless steel separation system.

Prior to adjusting parameters for a more defined separation using the stainless steel set-up, it was decided to test a solution that will mimicke a typical alkaline solution (0.5 to 1wt% NaOH) used in the conservation field to desalinate metal artifacts. With this aim, a 0.5 wt% NaOH (0.26M) solution with 1000 Cl^- ppm was prepared to be pumped through the column following the same separation procedure. Figure 13 display the results for a 0.5wt% NaOH and 1000 Cl- ppm solution.

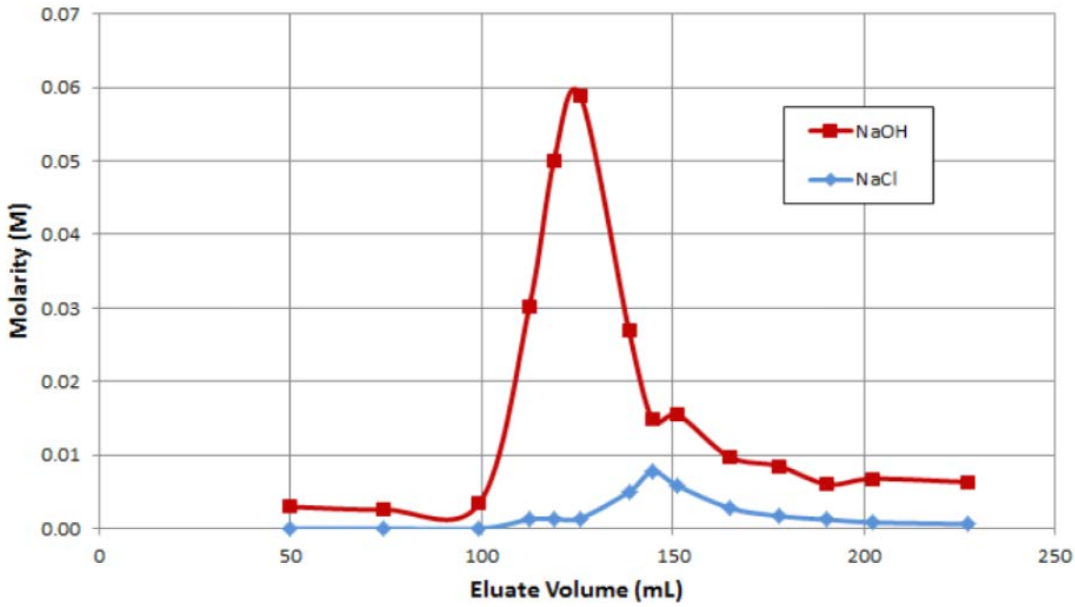

Figure 13: Separation results with a 0.5wt% NaOH (0.26M) and 1000 Cl^- ppm solution.

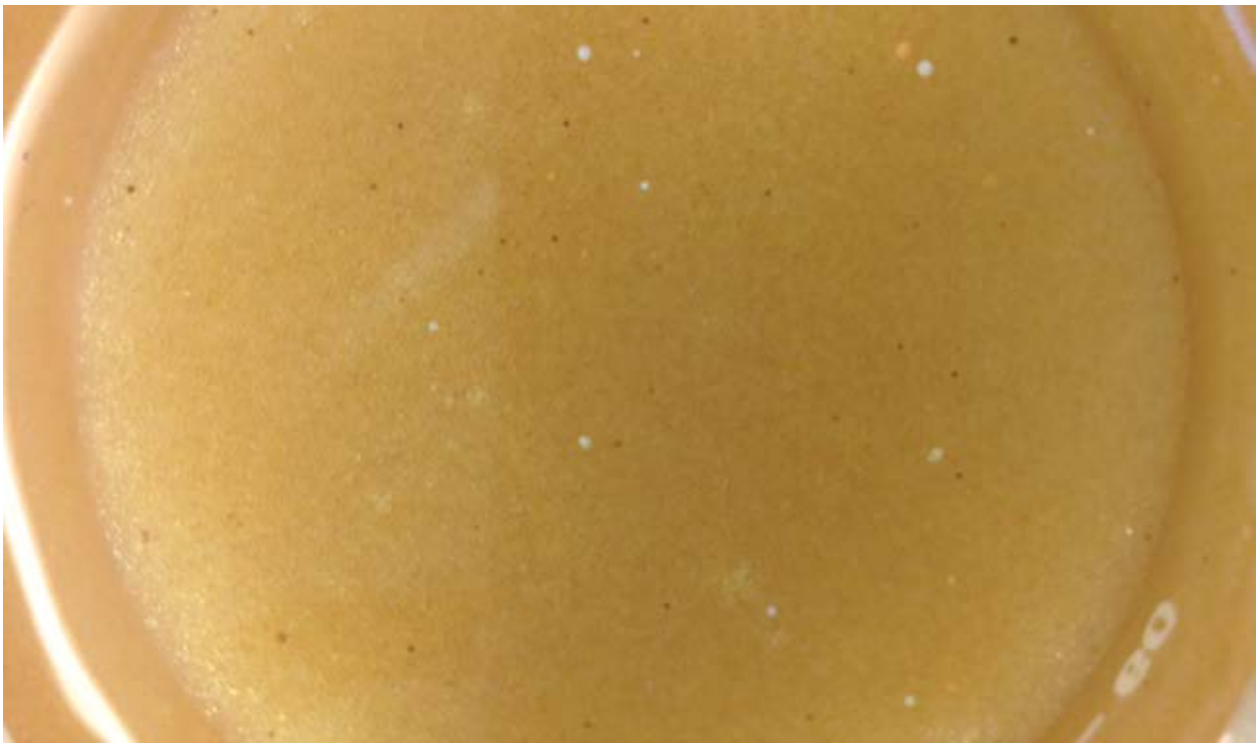

Figure 14: Fresh resin.

Figure 15: Expanded resin

The separation run had to be performed mutiple times due to issues with the resin behavior. While preparing a fresh resin bed and removing the existing resin from the column, it was noticed that the resin tended to expand and cluster, which definitely is not the expected behavior of a separation resin. The expansion behavior is highly noticeable when comparing Figure 14 and 15.

Figure 16 shows the results of the separation experiment with a fresh equilibrated resin bed.

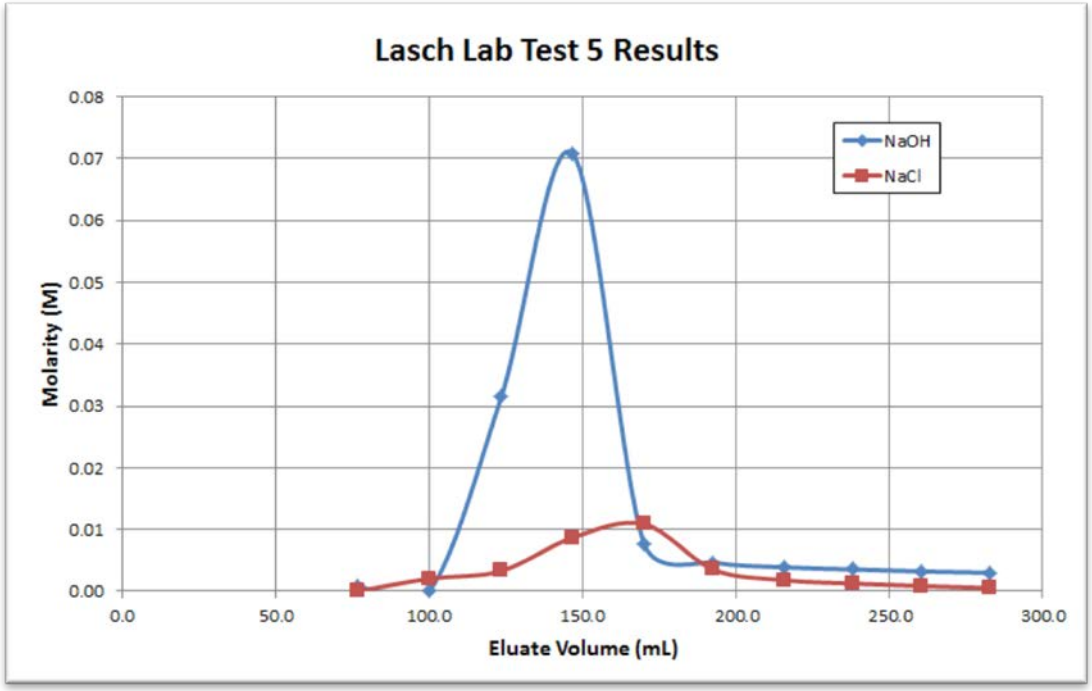

Figure 16: Typical separation results with a 0.5wt% NaOH (0.26M) and 1000 Cl^- ppm solution with a fresh equilibrated resin.

These results show that the resin is not separating low molarity solutions as well as it does for high concentration solutions. These results may mean the impossibility for use in the intended application as conservators generally work with low concentration solutions, not to exceed 1w% NaOH (0.53M).

Conclusions

The aim of this research was to develop a simple and effective method to improve the desalination treatments of archaeological iron. The application of retardation resin technologies to selectively remove chloride and other ions from alkaline solutions without significantly affecting pH was investigated. This technique was thought to improve the desalination process by being cost- and time-efficient and enhancing sustainability.

Prior to applying the technique to iron specimens, suitable ion-exchange resins were identified, and a particular resin called Dowex Retardion 11A8 was selected for its specificity in separating chloride ions from sodium hydroxide solutions in the pH range between 10 and 14.

Initial experiments were designed to reproduce a separation method published by The Dow Chemical Company, which is the manufacturer of the resin. The reported aqueous solution was about 2M NaOH and 2M NaCl. The duplication of the manufacturer's results, in terms of well-defined separation between NaOH and NaCl, was achieved in both glass column and stainless steel column set-ups. However, the concentrations of eluate were consistently lower or slightly lower than the ones reported.

Most importantly, for full integration of the retardation resin into a recirculation process applied to desalination in the conservation field, the caustic solution concentration had to be lowered from about 2M to 0.26M and not to exceed 0.53M. The results obtained with 0.26M (0.5wt%) NaOH solution were disappointing as the separation of NaOH and NaCl did not occur which is visible from overlapping peaks. These results prevent the use of the Dowex Retardion resin for the desalination of archaeological metal artifacts.

After further research into published studies, it appeared that the resin works only with high caustic solution concentrations, and no literature could be found on concentrations similar to the ones utilized in the conservation field. Finally, it should be noted that information regarding the Dowex Retardion 11A8 proved to be very scarce. It was limited to the manufacturer's website and few publications discussing the separation of nucleides.

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