Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

January 2010

Removal Of Perchlorate From Drinking Water And Ion-Exchange Regenerant Brines

Chulheung Bae
Electrochemical Design Associates Inc.

Brian Dougherty
Electrochemical Design Associates Inc.

Stephen Harrison
Electrochemical Design Associates Inc.

Follow this and additional works at: https://scholarworks.umass.edu/soilsproceedings

PART VII: Perchlorate

Chapter 15

REMOVAL OF PERCHLORATE FROM DRINKING WATER AND ION-EXCHANGE REGENERANT BRINES

Chulheung Bae, Brian Dougherty and Stephen Harrison
Electrochemical Design Associates Inc., 5705 Hollis Street, Emeryville CA 94608

Abstract: Perchlorate ions from rocket fuel, flare and munitions manufacture and use have escaped into groundwater in several states in the USA. Perchlorate causes alarm because it mimics iodine physiologically and is adsorbed by the thyroid gland, subsequently interfering with the endocrine systems of the brain. Removal of perchlorate to very low ppb is difficult on two fronts: competing ions such as nitrate, sulfate, carbonate etc. are often present at 1000 times higher concentration than perchlorate, and perchlorate is surprisingly stable considering its reputation as a rocket fuel oxidant. Direct electrochemical reduction of perchlorate in the parts per billion range is too slow and expensive to be viable. Ion exchange produces a troublesome disposal problem: either a perchlorate laden ion exchange resin or a brine stream containing high concentrations of perchlorate, nitrate, sulfate and bicarbonate. Electrochemical redox reduction of perchlorate, coupled to ion exchange capture and concentration is an economic and elegant method of dealing with both nitrate and perchlorate, particularly if the kinetics of the reduction process are fast. Perchlorate is surprisingly stable to reduction at a reducing cathode and with common reducing redox ions such as Cr^{2+}, Fe^{2+}. The reaction of perchlorate with Ti^{3+} is well documented in the literature, but the kinetics are slow in common solutions. In our latest study we have discovered that the reaction of perchlorate with titanium ions in methanesulfonic acid is very fast. We describe the laboratory experiments and pilot plant field trials in California that demonstrate the utility of this method for removing perchlorate and nitrate directly from drinking water and from regenerant brines from ion exchange systems.

Key words: perchlorate; ion-exchange; brine; removal; electrochemical destruction; groundwater.

1.   INTRODUCTION

Electrochemical Design Associates, Inc. has developed a series of electrochemical technologies to deal with toxic oxyanions in drinking water. Our target ions have been arsenic, nitrate, perchlorate, borate and chromate. Two of these technologies are now commercial and are described elsewhere (Clarke et. al. 2002; Clarke et. al. 2004). The common thread in these developments has been the use of electrons to collect and minimize the waste from the process by collecting or destroying the toxic anion. In this paper, the removal and destruction of perchlorate are described and discussed.

Perchlorate is a common constituent in rocket fuels and munitions manufacture and has escaped into the ground water in many states in the USA. This is causing alarm as perchlorate mimics iodine physiologically and is taken up by the thyroid gland in humans. The EPA has set a limit for perchlorate at 24.5 ppb; several states have set lower limits. California, in particular, has an action

limit of 6 ppb for drinking water supplies. In several parts of CA, notably the San Gabriel Valley region, perchlorate has been detected in the drinking water supply at concentrations as high as 50-100 ppb.

Remediation of ground waters and surface waters contaminated with perchlorate is difficult:

1. Removal is required down to parts per billion of perchlorate;
2. The ion is not easily destroyed in an aqueous environment;
3. Nitrate and other anions, which are usually present at concentrations several orders of magnitude higher than perchlorate compete with it during the reduction process.

Ion-exchange (IX) is one possible solution to the perchlorate problem. Non-selective IX resins can be used, but these merely transfer the perchlorate to a waste brine stream which must itself be treated or disposed of. In addition, these resins strip almost all ions from solution, so that the water produced while of high quality must have non-toxic ions added to reduce wear on the downstream piping & plant which deliver water to homes. Perchlorate selective IX resins have a high capacity for perchlorate, but these are not easily regenerated and must be disposed of after a single use.

Direct electrochemical reduction of perchlorate, that is in-situ reduction of perchlorate to chloride on an electrode even if possible, is too expensive, due to the limitations of dealing with very dilute target ions on a two dimensional surface, the electrode. This is a classical dilemma for electrochemical processing. As reactants become dilute mass transfer limitations of electrolytic reactions follows the path of diminishing returns as current efficiency declines and cell voltages increase.

The approach taken is to capture perchlorate by selective IX, concentrate it in the IX column regenerant, and then destroy the perchlorate via reduction to chloride using a redox agent present in the regenerant. The redox reagent can then be regenerated electrochemically, allowing the IX regenerant to be reused.

2.   DESCRIPTION OF TECHNOLOGY

2.1   Perchlorate Selective Ion Exchange

Perchlorate selective ion exchange media such as Purolite A530E and Rohm & Haas PWA2 have been widely demonstrated to have high selectivity and capacity for perchlorate. In drinking water applications, these media typically remove perchlorate and some nitrate from drinking water, but do not absorb other ions to any great extent. They are difficult to regenerate, however their capacity for perchlorate is high enough that a use once & discard philosophy is viable in some situations. A second advantage of these resins is that they can capture perchlorate from brine solutions, allowing an additional application for secondary treatment of waste brine regenerant streams from IX systems which use non-selective resins to treat perchlorate contaminated drinking water.

2.2   DePerc[TM]

EDA has developed a two stage process that elutes perchlorate from a perchlorate-selective IX resin and then reduces the eluted perchlorate to chloride using Ti^{3+}/Ti^{4+} redox chemistry. The Ti is cycled electrochemically, giving a closed loop process. This process is the subject of a US Patent Application (Clarke et. al, 2005).

3.   LABORATORY STUDIES

3.1   Column Studies

The laboratory phase of the work was performed primarily using column studies to determine the effectiveness of different reagents as regenerants. The IX resins used were Purolite's A530E and Rohm & Haas' PWA2 which offered high selectivity for perchlorate. These resins are considered to be single use resins due to their high selectivity for perchlorate, and are usualy incinerated once used.

3.1.1   Preparation of IX Columns

IX columns were prepared by weighing 20 g of the IX resin to be tested into a 2.5 cm diameter, 15 cm tall column. The resin bed depth was 5.5-6 cm. Deionized (DI) water was poured onto the media to assist the initial packing of the column. The resins were used as-received, with no pre-conditioning, other than rinsing with DI water. Between 20 ml and 50 ml of liquid, either the perchlorate inlet solution or DI water, was maintained over the beads at all times.

3.1.2   Loading Solutions

Loading solutions used in the lab phase of the study were prepared from DI water and sodium perchlorate ($NaClO_4.H_2O$, EM Science, AR grade). Due to the high capacity for perchlorate of the resins chosen, in order to minimize cycling times, loading solutions typically contained 40 mg/l perchlorate. This is 500-1000 times higher than perchlorate concentrations typically found in drinking water, and about 10 times higher than concentrations typically found in regenerant brines. Nevertheless, the data are still relevant since they demonstrated the effectiveness of the regeneration process.

3.1.3   Regenerant Solutions

Solutions tested as regenerants included baseline materials such as 20 wt% sodium chloride, 2M sulfuric acid, 4M methanesulfonic acid, and titanium salts of sulfuric and methanesulfonic acid (MSA). These were prepared by dissolving titanium oxysulfate ($TiOSO_4$, Alfa) in DI water, and then acidifying with either sulfuric or methanesulfonic acid (1M Ti, 4M H^+). The $TiOSO_4$ salt was supplied as a complex with sulfuric acid; the nominal composition was $TiOSO_4.2H_2O.H_2SO_4$. In addition, to eliminate the effect of sulfate, titanium powder was dissolved in methanesulfonic acid to give titanium methanesulfonate (1M Ti, 4M MSA).

3.1.4   Electrolysis of Ti Regenerant Solutions

A two-chamber electrochemical cell, constructed from polyethylene, was used to reduce the titanium in the regenerant solution from Ti^{4+} to Ti^{3+}. The anode was platinized titanium and the cathode was carbon felt attached to a titanium mesh current collector. The anolyte was 4M methanesulfonic acid; the catholyte was the regenerant solution. A Nafion membrane separated the anode and cathode chambers. Both anolyte and catholyte solutions were pumped through the cell at about 200 ml/min using a peristaltic pump. The nominal electrode surface area was 100 cm^2; the current was 4 A. The electrolysis proceeded with nearly 100% faradaic efficiency until most of the Ti^{4+} was reduced to Ti^{3+}; the end point can be detected by an increase in gas evolution and a change in the color of the solution.

This regenerant solution was used until 2 to 3 g of perchlorate had been desorbed from the IX resin; this was equivalent to 20% to 30% of the Ti^{3+} in solution. It was then returned to the electrochemical cell and electrolyzed until gas was evolved at the cathode. The regenerant was then used for additional regenerations.

3.1.5   Column Cycling

The perchlorate solution was pumped from the reservoir through the IX column from top to bottom, at a flow rate of 60-80 BV/hr. This corresponds to a flow velocity of about 3 m/hr. Loading continued until the perchlorate concentration in the effluent was equal to that of the influent. The resin bed was gravity drained, and the column connected to the regenerant system.

The regenerant solution was placed in a stirred, heated reservoir maintained at 45 °C throughout the regeneration. In most experiments, the regenerant was pumped from the bottom to the top of the column; i.e counter current to loading. The flow rate was about 60 BV/h and regeneration proceeded for 24-25 hours. The total volume of regenerant was about 30 BV. A few experiments were performed in single pass mode, and the effluent from the top of the column was collected in a separate container. The flow rate was the same as for the recirculating case, but the total number of bed volumes of regenerant used was larger, 120 BV.

After regeneration, the IX column was pumped dry of regenerant and rinsed with one to two BV of DI water to remove traces of the regenerant solution. This step was repeated until the pH of the effluent was between 3 & 4. Altogether, depending on how well the IX resin is drained each time, this requires 5 to 10 BV of DI water.

Samples were taken at intervals throughout the process and analyzed for perchlorate using Ion Chromatography.

3.2   Results & Discussion

The column tests used high inlet perchlorate concentrations as a means to speed up the loading process. A530E was loaded at 40 ppm influent perchlorate; PWA2 was loaded at 100 ppm for the first four cycles, and at 40 ppm for the others. Columns were loaded until the perchlorate concentration in the effluent equaled that in the influent. Whilst the difference between loading at 40 ppm and 100 ppm is not particularly significant, except that the equilibrium capacity of the resin will be slightly lower at 40 ppm, results at 40 ppm are not necessarily indicative of the capacity of the resin at lower concentrations of perchlorate.

Typical loading curves for Purolite A530E and Rohm & Haas PWA2 IX resins following regeneration via various regenerants are shown in Figures 1 & 2, respectively. It is apparent from these figures that the regeneration efficiency for both resins is fairly poor when NaCl, Ti[IV]OSO$_4$-H$_2$SO$_4$ or Ti[IV]OSO$_4$-MSA are used. For all three of these regenerants, A530E recovers about 35% of its initial capacity whereas PWA2 recovers about 10%. When the Ti[IV]OSO$_4$-MSA regenerant is reduced to its Ti[III] form, the regeneration efficiency of A530E improves to about 70%, however no change is seen for PWA2. The best result for both resins was obtained when the Ti regenerant is prepared directly from Ti powder dissolved in MSA. The regeneration efficiency of A530E was close to 100%, while that of PWA2 improved to 45%. It is also apparent from these tests that the A530E IX resin is more easily regenerated in general than the PWA2 resin. Note that the column reload for Ti[III]-MSA in Figure 2 has a lower inlet concentration than the other curves in this figure, so that it takes more bed volumes to load the column in this case.
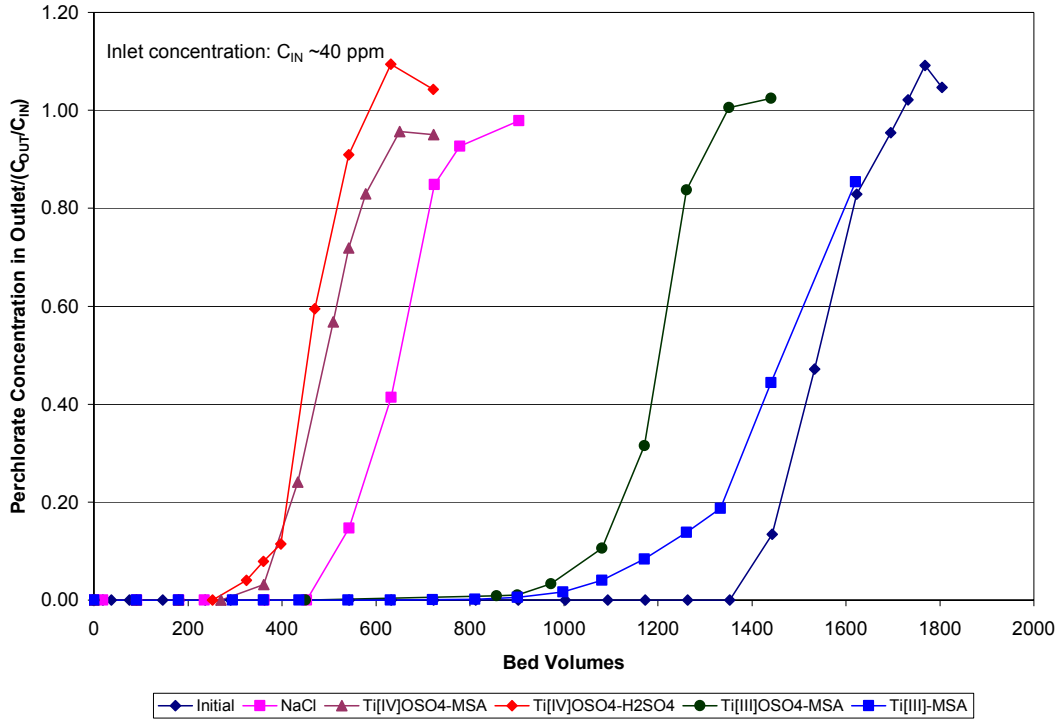
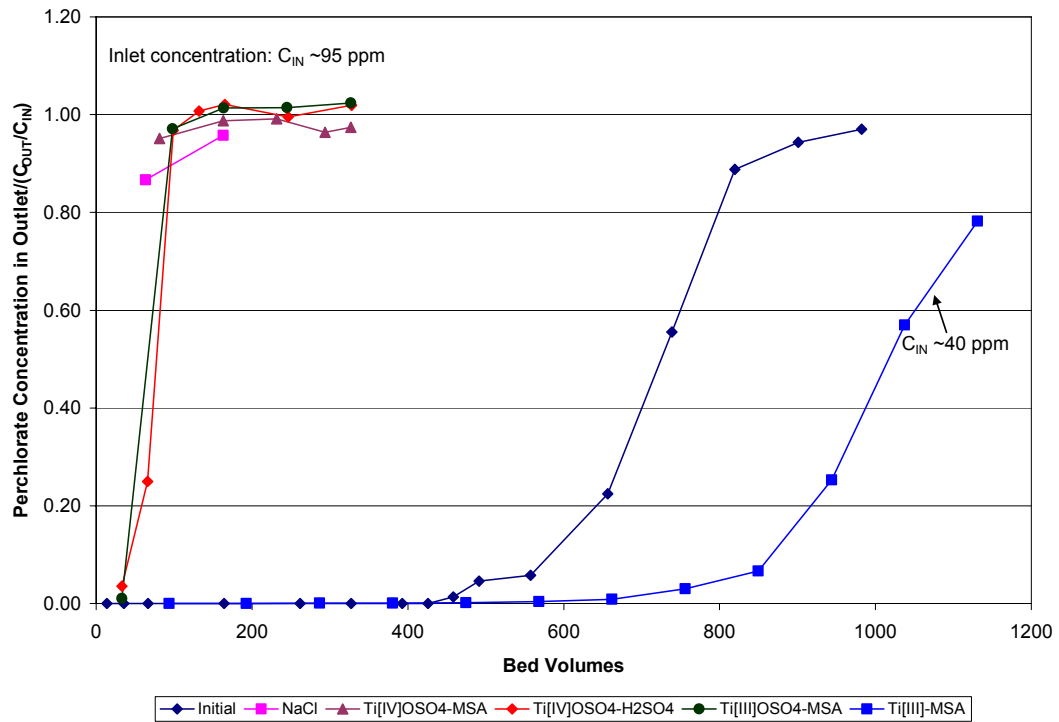*Figure 1.* Perchlorate loading curves for Purolite A530E IX resin

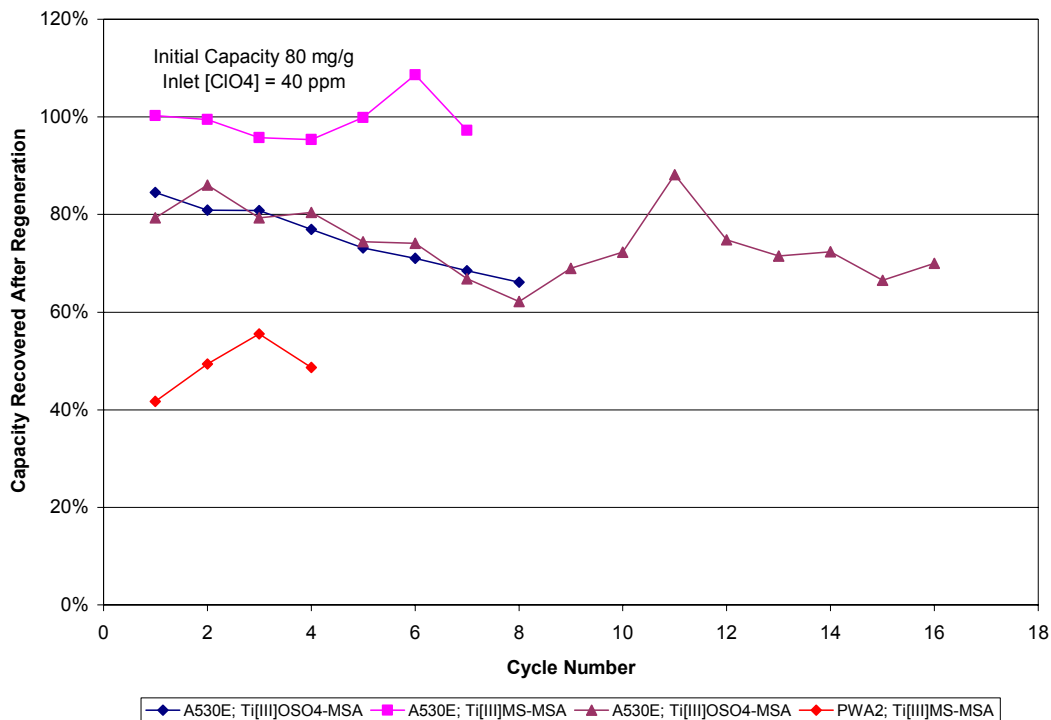*Figure 2.* Perchlorate loading curves for Rohm & Haas PWA2 IX resin

Figure 3. Capacity of IX resin on cycling

Figure 3 shows the effect of repeated cycling on the capacity of the two IX resins studied. For Ti[III]OSO$_4$-MSA, the efficiency of regeneration of A530E was about 80% on the first cycle, but decreased to about 70% after 8 cycles, where it remained through at least 16 cycles. Figure 3 shows the first eight cycles for two different columns of the A530E IX resin for this regenerant. After 8 cycles, one column was switched to TiMS$_3$-MSA. Using this regenerant, 95%-100% of the initial capacity was recovered through 8 cycles. For the PWA2 resin, the regeneration efficiency is about 50% using the TiMS$_3$-MSA regenerant, and varies a more during cycling.
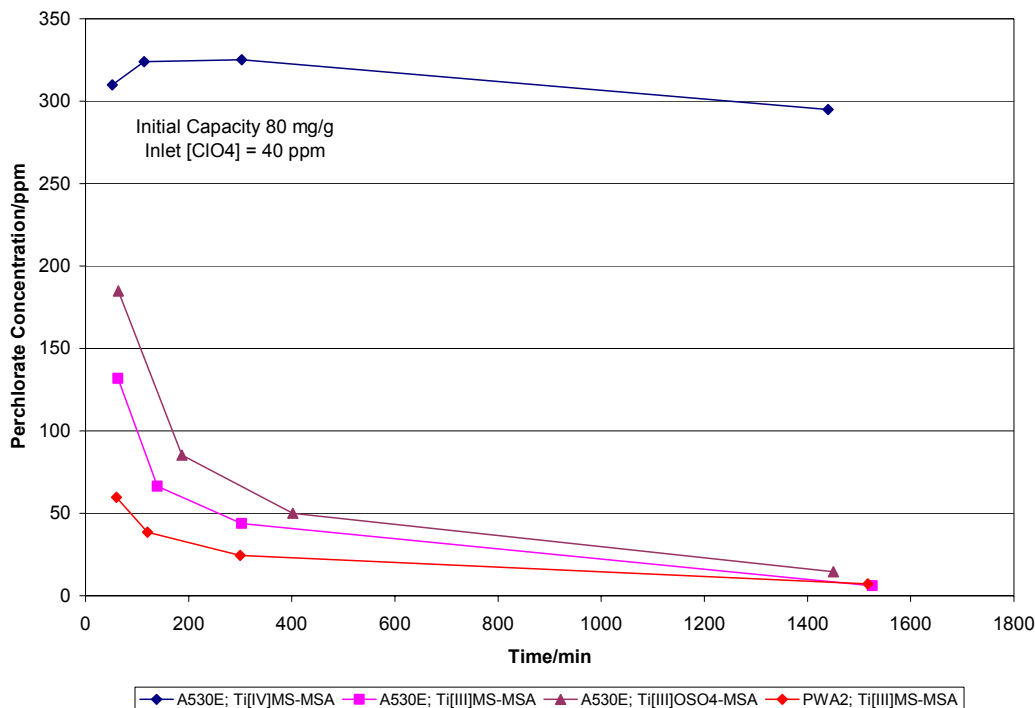
Figure 4. Perchlorate concentration in regenerant

Figure 4 shows the concentration of perchlorate measured in the regenerant during regeneration of the A530E resin. When the Ti[IV] form of was used, perchlorate was not reduced and reached a maximum concentration of 300-320 ppm after less than 60 minutes of contact with the IX resin. Presumably this represents the steady state concentration of perchlorate in the regenerant, for this resin, loaded at 40 mg/l perchlorate. When the Ti[III] version was used, the maximum perchlorate concentration was achieved at the start of the regeneration cycle, and decreased with time as the perchlorate is reduced, ultimately to chloride. The reduction in perchlorate concentration is significantly faster when only MSA is present (i.e. no oxysulfate), implying that the reaction rate between Ti^{3+} and perchlorate is faster in this case. For PWA2, the perchlorate concentrations are lower because the regeneration is less efficient.

4. PILOT-SCALE FIELD TRIALS

Baldwin Park Operable Unit LLC (BPOU) operates a water treatment system known as ISEP to remove perchlorate from groundwater as part of a process to produce potable water. This process generates a 25-70 gpm waste brine stream that contains 4 to 5 ppm perchlorate in addition to other ions. This waste stream is currently untreated and sent to the local sewer. Regulatory changes in the near future mean that this practice needs to be modified, and the perchlorate must be removed from the brine prior to discharge to the sewer.

4.1 Pilot Plant Description

In collaboration with Rohm & Haas, an IX system was designed to remove perchlorate from the brine waste stream using Rohm & Haas's PWA2 perchlorate selective resin. Figures 5 through 7 are pictures of this system as installed at BPOU. The system comprised two 1.3 ft^3 IX vessels, each containing 1.1 ft^3 of resin. The columns were operated in series. Only the first column was regenerated; the second was used as a polishing column. The objective of the test was to operate the system through ten regeneration cycles with no perchlorate leakage from the second IX unit.

Figure 5. Ion-exchange subsystem of unit deployed at Baldwin Park

Waste brine from the ISEP process was preconditioned by feeding it into a holding tank to allow dissolved gasses (mainly carbon dioxide) to escape. It was then pumped through the ion exchange system at an average flow rate of 38 BV/h. After loading for eight hours, the first second IX column was isolated from the rest of the system, and the first IX column was drained of brine and connected to the regenerant system. Regenerant was pumped from its storage tank through the first IX column for 16 hours. At the end of the regeneration cycle, the regenerant was displaced back to the storage tank using DI water. Column 1 was then rinsed with DI water, and ready for the next cycle.

Figure 6. Electrochemical destruction unit for regenerant recycle

The regenerant was recycled by electrolysis in the electrochemical destruct unit (EDU). The EDU was essentially a larger sized version of the lab cell described above. For this demonstration, the regenerant was prepared from the $TiOSO_4$ salt described earlier, acidified with methanesulfonic acid.

4.2   Results & Discussion

Three series of tests were run at BPOU. The first two series demonstrated that perchlorate could be removed from brine using selective ion-exchange, that the IX resin could be regenerated, and that the perchlorate could be destroyed in the regenerant. However, these two series did not meet the project objective due to premature leakage of the perchlorate. This was due in part to poor design of the IX system and because of contamination of the IX resin. Thus the system was redesigned before the third series of experiments.

The perchlorate concentrations at the inlet and the outlets to each of the IX columns during the third series of tests are presented in Figure 7 with respect to elapsed loading time. It should be remembered that loading cycles lasted for eight hours, so Figure 7 summarizes the results for all ten cycles.
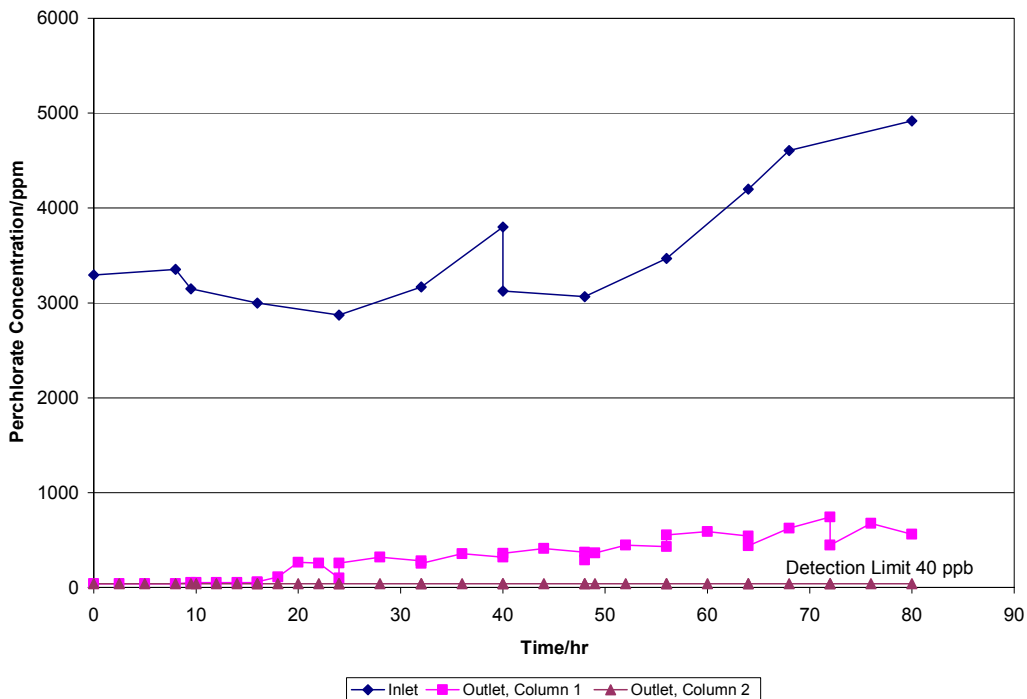
Figure 7. Perchlorate concentrations in brine during loading cycles

The feed concentration ranged from 3000 ppb to 5000 ppb, and was higher towards the end of the test, especially the last three cycles. The concentration of perchlorate in the outlet from the second IX column was less than 40 ppb, the detection limit for this trial. (The detection limit of the IC is 4 ppb, but the high background conductivity of the brine matrix requires a dilution factor of ten to obtain quantitative data, hence the 40 ppb detection limit).

The perchlorate concentration at the outlet from the first IX column was at the detection limit for the first two cycles, but subsequently the bleed increased to about 600 ppb by cycle 8, at which point it stabilized during the last two cycles despite the higher inlet concentration. Figure 8 shows the bleed rate as a percentage of the inlet concentration. The small amount of bleed shown in these data is typical of a process in which the column is undergoing an incomplete regeneration. It also appears from the data that the bleed rate has begun to approach a steady state, although more cycles are needed to confirm this. The perchlorate leaking from column 1 can therefore be captured on a second ion exchange unit which could be regenerated or disposed of, depending on economics.
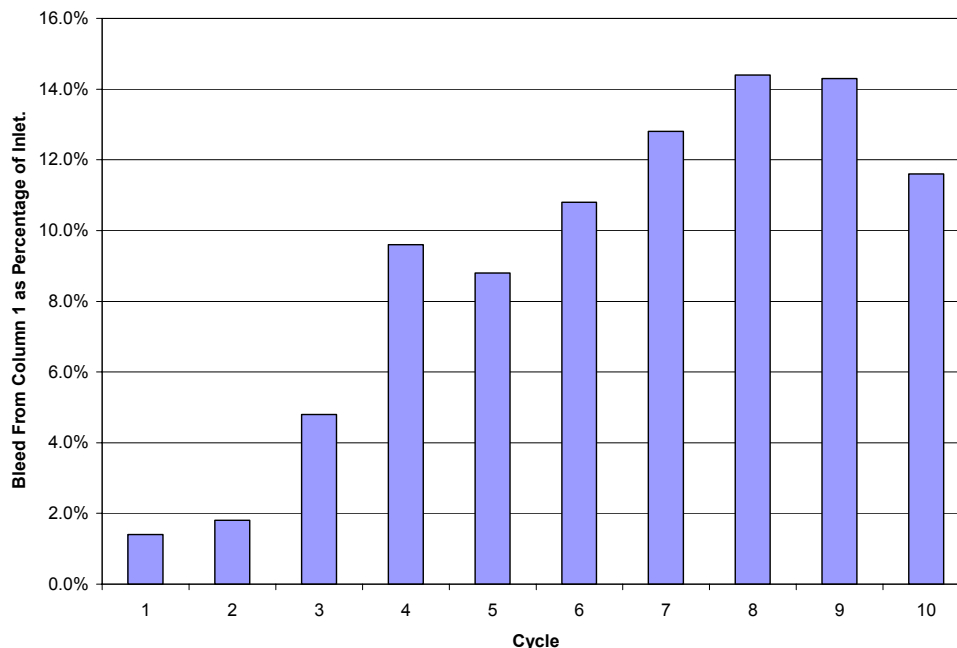
Figure 8. Bleed of Perchlorate From IX Column 1

During this series, the average inlet concentration of perchlorate was 3.6 ppm perchlorate. Given the flow rate (19 lpm) and total operating time (80 hours), the total volume treated was around 91,000 liters. Therefore, the total quantity of perchlorate passed through the IX system was 328 g. Analysis of the resin from the two IX columns following the test showed that the amount of perchlorate remaining on column 1 was 1.5 g/l of resin, or 57 g, and the amount remaining on column 2 was 0.78 g/l or 23 g. Thus of the 328 g of perchlorate which entered the system, 80 g remained on the columns while 248 g of perchlorate was removed during regeneration. This would be the equivalent of 70 ppm perchlorate in the regenerant (3500 liters) if the perchlorate did not react with Ti, well above the 1.2 ppm detection limit for this solution. No perchlorate was detected in the regenerant. It can therefore be concluded that the ion-exchange resin was regenerated, and that a significant portion of the perchlorate captured by the resin was destroyed during the process.

5.   CONCLUSIONS

On the basis of these data, the demonstration achieved the project success criteria (zero bleed from column 2). It is however recognized that the process needs further improvement, in particular to minimize bleed from Column 1 so that the size of any polishing column can be reduced. In particular, a more complete regeneration of the IX resin would lower the bleed significantly. It should be noted that the regenerant used in the field study was not the best one from the lab data, due to the lack of commercially available TiMS$_3$ salts.

In our opinion, the process has been successfully scaled-up from the laboratory in the most difficult of effluents – perchlorate-containing brine. The process is even more effective when used with water rather than brine. In this case the perchlorate leakage is non-existent and a polishing column, though desirable, is not essential to the process.

174 *Contaminated Soils- Perchlorate*

ACKNOWLEDGEMENTS

REFERENCES

Clarke S.R., Clarke R.J., Murdock R., Butler, C., Mohanta, S. 2002. Water Treatment Method and Apparatus. US Patent #6383395.

Clarke R.L., Harrison, S., Jain, S. 2004. Electrochemical Nitrate Destruction. US Patent Application PCT/US2004/042961 B1

Clarke R.L., Harrison, S., Dougherty, B.J., 2005. Perchlorate Destruction. US Patent Application PCT/US2005/0239632 A1