A Method for Removing Ammonium Ions From a Subterranean Formation After In-Situ Uranium Leaching

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Summary

Ammonium carbonate and bicarbonate are the preferred carbonate sources in alkaline in-situ leaching of uranium. The ammonium ion exchanges into the clay in the formation and is difficult to remove during restoration operations. A new process is proposed which holds the potential for rapid and effective reduction of ammonia in the formation and groundwater to acceptably low levels. The process employs pH-adjusted, chlorinated water to decompose the ammonia quantitatively. The operation involves flushing the formation with connate water or brine, injecting chlorinated water, and finally flushing with connate water. This process is effective in laboratory tests.

Introduction

In-situ leaching, or solution mining, is now emerging as a viable technique for recovering uranium from some low-grade ore bodies.[1,2] As a result, several pilot and commercial in-situ leaching plants are in operation in south Texas – e.g., Mobil Oil Corp., Intercontinental Energy Corp., Wyoming Minerals Corp., Union Carbide Corp., and U.S. Steel Corp.

Leaching systems are classified conveniently as either acidic or alkaline. For sandstone ores containing substantial quantities of carbonates, alkaline leaching is preferred. The alkaline leach solutions contain an oxidant (H_2O_2, $NaClO_3$, or O_2) and a mixture of carbonates. Ammonium carbonates have been the most popular source of carbonates. This type of leaching formulation has been used sucessfully in south Texas.

Since the ore bodies generally contain up to 20% or more of cationic exchangeable clays, the NH_4^+ in

the leach solution exchanges with the cations in the clay according to the following equations.

$$Na \cdot clay + NH_4^+ \rightleftharpoons NH_4 \cdot clay + Na^+.$$

$$Ca \cdot clay + 2NH_4^+ \rightleftharpoons (NH_4)_2 clay + Ca^{++}.$$
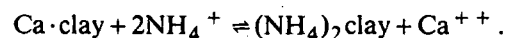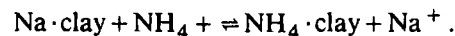
The selectivity of clays for NH_4^+ is high, and the NH_4^+ ion exchange capacity of the ore may become quite high depending on the overall clay content. A typical NH_4^+ ion exchange isotherm is presented in Fig. 1, which shows, for example, that for a leach solution containing 10g/L of NH_4HCO_3, the equilibrium concentration of NH_4^+ on the ore is 0.14 meq/g, equivalent to an NH_3 concentration of 0.24% of NH_3 in the ore body. At the conclusion of the leach operation, the formation is contaminated with this great quantity of NH_4^+ ion. If not removed, the NH_4^+ ion will release slowly by exchanging with the incoming cations in the aquifer, resulting in pollution of the groundwater.

Government regulations require that water in the leached formation be restored substantially to its original quality. Furthermore, the current Texas Dept. of Water Resources permit procedures require groundwater restoration be completed immediately upon completion of mining of the site.[3] Although baseline levels for NH_3 are not set yet, levels in the 10-ppm range have been suggested. Since the ammonia is exchanged into the clays chemically, it cannot be flushed out readily and requires counter ions, such as Na^+ or Ca^{++}, for removal by ion exchange. Furthermore, the ion exchange equilibrium limitation makes the restoration of the desired low level difficult and time consuming.

To speed up the restoration process, a restoration fluid with high salt content of NaCl or $CaCl_2$ can be used. To speed up the restoration process further, a

restoration fluid comprising an aqueous solution of a strong soluble alkaline compound, such as NaOH, can be used.[4] However, while these approaches work well for some ore bodies, they require a substantial quantity of chemicals and produce a large quantity of waste water containing ammonia which has to be disposed of properly at the surface. Furthermore, in some instances the use of caustic solution as the restoration fluid may require the addition of a salt such as sodium chloride[5] to prevent clay swelling and, hence, resultant loss in formation permeability.

In this paper, a technique is presented which holds the potential for rapid and effective removal of ammonium ion from the formation during groundwater restoration.

Technique

The proposed technique for removing ammonium ions comprises the following three steps.[6]

1. Flush the leached formation with connate water to remove ammonia and other dissolved solids from the pores.
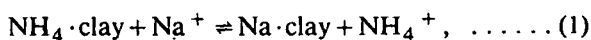
2. Inject the required amount of chlorine water or hypochlorite solution at pH of 8 to 10. The produced water is made up with chlorine or hypochlorite for recycle.

3. Flush the formation to lower the total dissolved solids to the desired level.
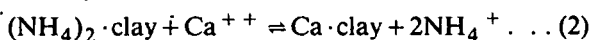
In the following sections, the theoretical basis of the process, the reactions involved, and the mechanism of ammonium ion removal are discussed and confirming laboratory experiments are described.
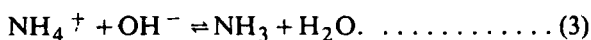
Reactions of Ammonia With Chlorine and Hypochlorite

The equilibria between NH_4^+ in the clay and other cations such as Na^+ in the formation or restoration fluid are represented by

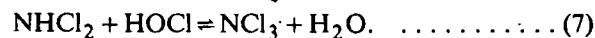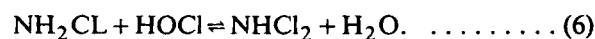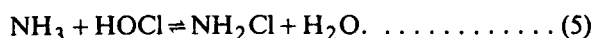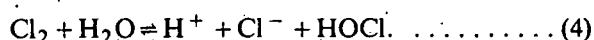$$NH_4 \cdot clay + Na^+ \rightleftharpoons Na \cdot clay + NH_4^+, \quad \ldots \ldots (1)$$

or

$$(NH_4)_2 \cdot clay + Ca^{++} \rightleftharpoons Ca \cdot clay + 2NH_4^+ . \ldots (2)$$

In turn, the NH_4^+ ion is in equilibrium with NH_3:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O. \quad \ldots \ldots \ldots \ldots (3)$$

As the pH of the system is increased, Eq. 3 is shifted toward the right to form more NH_3 and decrease NH_4^+. This, in turn, shifts Eqs. 1 and 2 toward the right to facilitate NH_4^+ removal from the clay. The NH_3 in the formation then is reacted with chlorine or hypochlorite.

These reactions are of great importance in water treatment. Chlorination of drinking water for disinfection is used widely by many municipalities. However, the reactions are not well understood. The reactions are presumed to proceed in the following sequence.[7,8]

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl. \quad \ldots \ldots \ldots (4)$$

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O. \quad \ldots \ldots \ldots (5)$$

$$NH_2CL + HOCl \rightleftharpoons NHCl_2 + H_2O. \quad \ldots \ldots \ldots (6)$$

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O. \quad \ldots \ldots \ldots (7)$$

$$2NCl_3 \rightarrow 3Cl_2 + N_2. \quad \ldots \ldots \ldots \ldots \ldots \ldots (8)$$

The Cl_2 reacts with water to form hypochlorite, with which NH_3 starts to react. The overall reaction between NH_3 and chlorine can be written as follows.

$$2NH_3 + 3Cl_2 \rightarrow 6H^+ + 6Cl^- + N_2\uparrow. \quad \ldots \ldots \ldots (9)$$
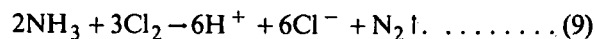
Note that Eqs. 4 through 7 are reversible, while the decomposition reaction (Eq. 8) is irreversible, leading to the possibility of complete removal of NH_3 without equilibrium limitation. The approximate equilibrium constants for the preceding reactions have been presented by Drago.[9]

Studies of the rates of decomposition of the chloramines have shown that, depending on the pH and the reaction step, the second-order rate constants at 25°C are high and in the range of 10 to 10^4 $L \cdot mol^{-1} \cdot s^{-1}$.[10,11] Preliminary results from this laboratory showed that the reaction between hypochlorite and ammonia and ammonium ions in both aqueous solution or on clay can be completed in less than 10 minutes. The contact time between the restoration fluid and ammonium-containing formation (or number of days to pump through 1 PV of fluid) is typically 2 to 4 weeks. Therefore, reaction between hypochlorite and ammonia and the decomposition reaction of chloramines can be considered instantaneous in the time scale for groundwater restoration operations.

Alternatively, the NH_4^+ may react directly with hypochlorite to form nitrogen and chloride ion.

As pointed out, the last reaction in the sequence involving ammonia and chlorine or hypochlorite is irreversible, making it possible to carry the overall reaction to completion. This is one of the most important features of this process. When caustic or lime water is used to remove ammonia, the process is limited by the equilibrium described and by the law of mass action. This makes restoration of groundwater to acceptable ammonia levels extremely difficult. Based on the ion exchange isotherm in Fig. 1, we have estimated that 99.5% of the NH_4^+ ion in the clay has to be exchanged with other cations such as Ca^{++} or Na^+ to restore the ammonia in the groundwater to a stable level of 3 ppm or lower.

In summary, chlorine water or hypochlorite injected into the formation would react with ammonia in equilibrium with the ammonium clay through a series of reactions to form harmless nitrogen gas. The reactions are fast enough to be considered instantaneous. The overall reaction is irreversible and makes complete removal of ammonium ion possible.

Experimental

The efficiency of chlorinated water as a restoration fluid was studied in laboratory column tests using 1-cm-ID, 30-cm-long glass columns packed uniformly with 18 cm^3 (23.4 g) of the uranium ore. The top and the bottom of the columns were filled with 3 cm^3 each of 100-200 mesh fine quartz to ensure uniform flow of the liquid through the bed. The uranium ore
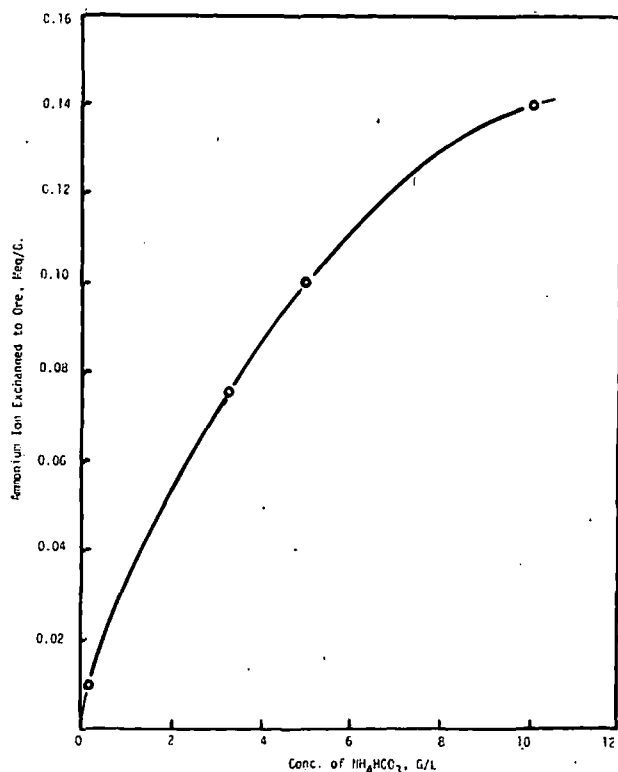
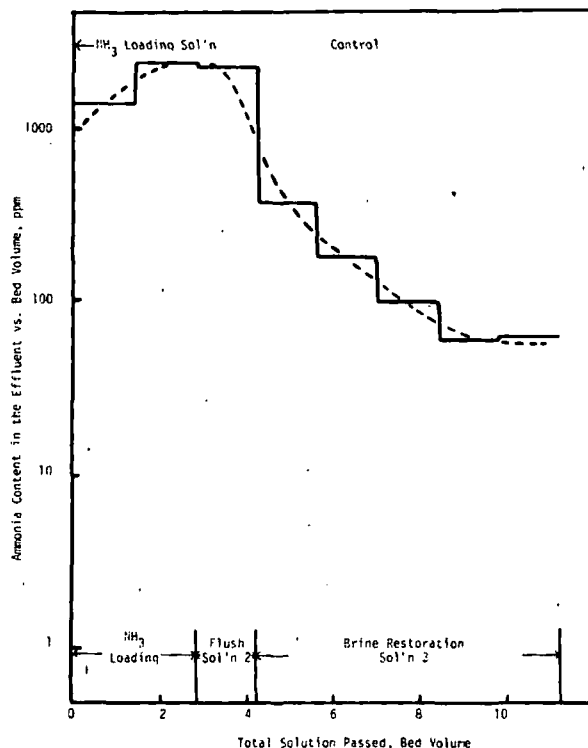**Fig. 1** – Exchange isotherm of ammonium ion on ore.

Fig. 2 – Ammonia content in the effluent vs. bed volume.

was obtained from the Catahoula formation of the Texas coastal plain. The clay content was about 20 wt%, mainly in the form of smectite (montmorillonite). Its ion exchange capacity for NH_4^+ was 0.15 meq/g.

The solutions used were prepared by adding CP-grade chemicals to distilled water. Chlorinated water was prepared by saturating the solutions with chlorine gas at 1 atm. The composition of the various solutions used are shown in Table 1. The final pH of the solution was adjusted to the level indicated. ·

The packed columns first were loaded with NH_4^+ ion by pumping 2.8 bed volumes of Solution 1 (Table 1) to simulate the leaching operation. In this experiment, 1 bed volume of solution is .18 cm^3. At the end of this loading step, the ore was saturated with ammonia as indicated by the ammonia concentration of the effluent, which was equal to that of the feed, Solution 1 (Fig. 1). The loaded columns then were flushed with 1.4 bed volumes of flushing Solution 2 (Table 1), which simulates the connate water normally present in the natural formation.

The columns thus prepared were restored as follows.

Col. 1. The control column was flushed with 7 bed volumes of restoration fluid, Solution 3 (Table 1).

Col. 2. The column was flushed continuously with 5.6 bed volumes of chlorinated water, Solution 4.

Col. 3. To simulate slug injection, 2.8 bed volumes of the chlorinated water, Solution 4, were injected. This was followed by injection of 2.8 bed volumes of chlorine-free restoration fluid, Solution 3.

To facilitate direct comparison of its efficacy for ammonia removal with the conventional high-brine flushing, the chlorinated water (Solution 4) was prepared by adding chlorine to the high-brine restoration fluid (Solution 3). In the proposed scheme the formation water, rather than the high-brine solution, will be used in preparing chlorinated water.

The process of NH_4^+ removal was followed by collecting samples of the effluent every 1.4 bed

· **TABLE 1 – COMPOSITION OF SOLUTIONS USED**

Component	Solution 1,* Ore Pretreating	Solution 2, Flushing	Solution 3, Restoration	Solution 4, Chlorination
NaCl, g/L	5.0	5.0	20	20
NH₄HCO₃, g/L	3.0	–	–	–
NH₄OH, g/L	5.8	–	–	–
Cl₂, g/L	–	–	–	6.3**
pH†	9.4	8.0	10.0	10.0

*NH₃ content was 2,670 ppm by analysis.
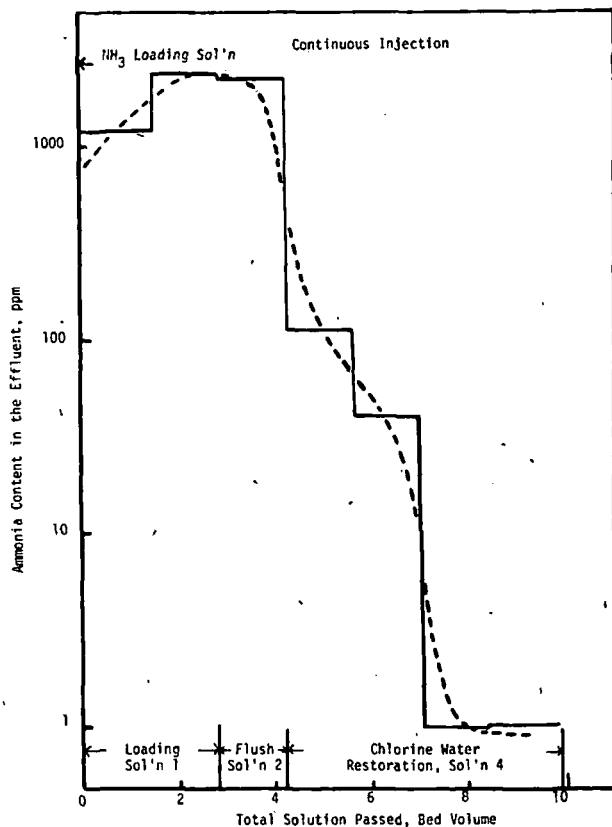**Based on chlorine solubility.[12]
†pH adjusted.

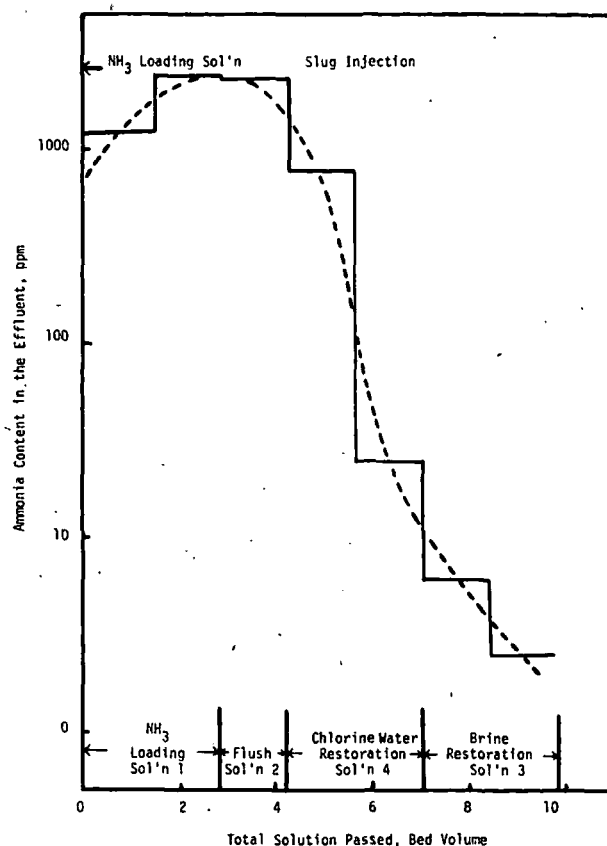**Fig. 3 — Ammonia content in the effluent vs. bed volume.**

Fig. 4 — Ammonia content in the effluent vs. bed volume.

volumes and analyzing for NH_3. Ammonia was determined using an ammonia electrode. This method is acceptable to U.S. federal and state agencies for analysis of ammonia in water. Note that in this test, both free NH_3 and NH_4^+ ion in the solution are included in the determination.

Results and Discussion

The results are shown in Figs. 2, 3, and 4 by plotting the ammonia content of the effluents against the total bed volumes of restoration fluid passed through a respective column.

Efficacy of Chlorine Water for Removing Ammonia

A comparison of Figs. 3 and 4 with Fig. 2 shows that chlorine was effective in lowering ammonia. In addition, it takes small quantities (in terms of bed volumes) of chlorine water to achieve levels of ammonia removal. In the continuous mode, 3 bed volumes of chlorinated water brought the ammonia level in Col. 2 from 2,600 ppm down to the target level of 3 ppm, while the ammonia content of the effluent from the control run was still 130 ppm after 3 bed volumes. Furthermore, the rate of ammonia removal fell off rapidly in the control run, suggesting the difficulty of ammonia removal to a low level in accord with the rationale described previously.

Mode of Chlorine Water Injection

In Col. 3, the chlorine water was injected as a slug.

After 1.4 bed volumes of flushing fluid, 2.8 bed volumes of the chlorinated water were injected, followed by 2.8 bed volumes of chlorine-free restoration fluid (Solution 3). The ammonia content of the effluent was down to the target value of 3 ppm after a total 4.6 bed volumes were passed. Thus, it may be feasible to inject chlorine water in the form of a slug to reduce operation costs.

Mechanism of Ammonia Removal

To remove ammonium ions from the clay and to reduce the ammonia in the produced water, there are two mechanisms: (1) cationic exchange between ammonium ion in the clay and cations (e.g., Na^+) in the groundwater and (2) decomposition of ammonia with chlorine or hypochlorite. In a column test or field operation, both of these mechanisms are operative. During the early stages of restoration, the injected chlorine reacts rapidly with the ammonia. The chlorine-depleted restoration fluid continues to move downstream and continues to remove ammonium ion by cationic exchange. The ammonia released from the clay is produced in the effluent. However, as more chlorinated water is injected, there is more chlorine to react with ammonia, resulting in very low levels of ammonia in the effluent. In the early stage of restoration when ammonia level is high, a large quantity of ammonia can be removed by flushing with connate water and ion exchange with chlorine-free brine solution. To minimize con-

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sumption of chlorine, the formation can be flushed with connate water and ion exchanged with brine solution before injecting chlorinated water.

The reaction rate between ammonia and hypochlorite is high, as suggested by the preliminary results mentioned. There was no breakthrough of hypochlorite while there was any detectable ammonia in the effluent.

Chlorine Requirement

The chlorine requirement for this restoration process depends on three factors: the amount of ammonium ion in the formation when the chlorine water injection is started, the stoichiometry of the reaction between ammonia and chlorine, and the selectivity of chlorine for ammonia. As a result, the chlorine requirement is rather ore specific.

If the reaction sequence shown is correct and the selectivity for NH_3 is unity, it takes 1.5 mol of Cl_2 to decompose 1 mol of NH_3 (Eq. 9) corresponding to 6.3 lbm of Cl_2 per 1 lbm of NH_3. In actual field operation, it may take somewhat more chlorine to compensate for side reactions.

Although the column data in this study are not exact enough to determine the chlorine consumption, an estimate was made by means of ammonia and chlorine balances. For this estimation, the following assumptions were made.

1. The ammonium ion content in the formation after connate water flushing is 0.14 meq/g, as expected from the ion exchange isotherm.

2. The ammonium ion either is produced in the effluent or is decomposed by chlorine.

3. Chlorine content in the formation up to 2.8 bed volumes of injection is nil.

The results are 6.0 and 8.4 lbm of chlorine per 1 lbm of NH_3 for the continuous and slug injection model, respectively (Table 2). The difference in the chlorine consumption between these two runs is relatively large, but this is believed to be within the expected limits of experimental accuracy.

Note that the crude chlorine consumptions are not too far from the theoretical value of 6.3 lbm per 1 lbm of NH_3. Therefore, it is most likely that the chlorine would react selectively and quantitatively with ammonia underground, and the stoichiometry based on the reaction sequence described is a good guide to estimate chlorine consumption.

There are compounds in the ore body which can be oxidized by hypochlorite, such as pyrite, molybdenum, and organic carbon. These reducing compounds can compete with NH_3 for hypochlorite to increase the chlorine requirement. Fortunately, the selectivity of dilute chlorine water for NH_3 is very high, as indicated by the results shown. Furthermore, when this process is applied to leached ore bodies, most of easily oxidizable compounds such as molybdenun and pyrite in the flowing channels already will have been oxidized.

In a series of separate experiments, it was found that after flushing the columns for 10 days with 5 PV of dilute chlorinated water, the NH_3 content of the effluent was reaching very low levels but no sulfate

TABLE 2 — CHLORINE CONSUMPTION

	Col. 2, Continuous Injection	Col. 3, Slug Injection
Initial NH_4^+ in formation as NH_3, 10^{-2} g	5.69	5.69
NH_3 produced,* 10^{-2} g	0.46	1.94
NH_3 decomposed, 10^{-2} g	5.23	3.75
Chlorine injected, 10^{-2} g	31.5	31.5
Chlorine consumption, g/g	6.0	8.4

*During the 2.8 bed volumes of chlorine water injection.

ion could be detected. Complete oxidation of pyrite would have led to sulfate ion. Sulfate ion did break through after 7 PV when the NH_3 essentially was exhausted. These results suggest that much of the chlorine injected to the formation could travel through the formation to react with NH_3.

Conclusions

Ammonium carbonate and bicarbonate are favored as the source of carbonate for alkaline in-situ leaching of uranium. Upon completion of the leaching operation, the formation and groundwater have to be restored to near the baseline quality levels. Ammonia is difficult to remove in this restoration process, and current restoration procedures are either difficult to employ due to formation permeability loss or require many pore volumes of restoration fluid. A process is proposed which has the potential for rapid and effective reduction of ammonia in the groundwater to very low levels,

The restoration process involves three steps: (1) flushing the formation with formation water or brine, (2) injecting pH-adjusted chlorinated water or hypochlorite and producing an equal amount of water at the production well, and (3) again flushing the formation with connate water.

The process is effective in laboratory column tests, where less than 3 bed volumes are required to lower the ammonia level from 2,700 to 3 ppm, but has not been tested in the field. The chlorinated water can be injected continuously or in the form of slug, as long as sufficient chlorine is injected. In the absence of other reducing compounds in the formation, the chlorine consumption is estimated to be about 6 lbm per 1 lbm of NH_3. To minimize chlorine consumption, restoration can be started with connate water flushing and brine ion exchange to remove the initial, easily removed ammonia.

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SI Metric Conversion Factors

$$\text{atm} \times 1.013\ 250^* \quad E+02 \quad = \text{kPa}$$
$$°F \quad (°F-32)/1.8 \quad\quad\ \ = °C$$
$$L \times 1 \quad\quad\quad\quad\quad\quad\ = \text{dm}^3$$
$$\text{lbm} \times 4.535\ 924 \quad E-01 = \text{kg}$$

*Conversion factor is exact.

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