



Lead/carbon steel galvanic corrosion evaluation

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Abstract

In a study aimed to select a carbon steel for its possible use as a liner for a high level radioactive waste canister, galvanic corrosion tests of lead/carbon steel galvanic couples in groundwater and in seawater were performed at 75°C. Lead behaved anodically due to a current polarity inversion phenomenon, and therefore corroded preferentially. This polarity inversion is temperature dependent. Under the same conditions, commercial lead showed higher corrosion rates in groundwater than high purity lead. No current polarity inversion was detected in galvanic tests performed either in bentonite suspensions in groundwater or in seawater.

1. Introduction

In the original Argentine repository project, based on the concept of multiple barriers to assure a long term isolation from the biosphere, lead was chosen as one of the metal components for the high activity nuclear waste canisters.

According to that project, the canister will have a thick lead wall, this metal being selected due to its good radiological protection quality and corrosion resistance. The canister will also have a thin external liner of a metal or alloy to be chosen. The repository will finally be located in granitic rock. Bentonite and a bentonite/sand mixture will be used as backfilling once the container is placed in the repository rock hole. Temperature of the rock, once the repository is completed, will be 60°C, while the canister external surface temperature is expected to reach 75°C.

Lead corrosion behavior in groundwater and in other corrosive environments has already been studied [1,2]. High purity lead showed good corrosion behavior in natural groundwater, the corrosion rate being of the order of micrometers per year (0.001 mm/year at 75°C) [2]. This good corrosion performance is due to the presence of a basic lead carbonate passivating film on the lead surface

[3]. Lead corrosion is affected mainly by some types of salts present in the environment. Nitrates and acetates induce high lead corrosion rates [4]. Chloride effect depends on its concentration; very low chloride concentration (5×10^{-4} M) produces lead corrosion rates almost as high as those found with distilled water (0.56 mm/year) [1]. This corrosion rate decreases with the increase of chloride concentration [5,15].

Lead corrosion resistance depends also on the presence of lead galvanic pairs with a more noble metal. This galvanic corrosion may occur in the probable event of a small failure in the canister external wall. This failure could thus produce the simultaneous exposure of the inner lead barrier and the external metal to groundwater. Considering this possibility, the corrosion behavior of lead/metal galvanic couples was studied at different temperatures, in order to select the metal for the canister external wall.

Preliminary titanium/lead and AISI 304 stainless steel/lead galvanic tests were performed in groundwater and in 10% bentonite suspensions in groundwater [5]. These tests showed that titanium and stainless steel behaved always as a cathode, promoting the lead galvanic corrosion. Passive stainless steels behaved as noble metals in the galvanic series. Besides, stainless steels are generally susceptible to pitting corrosion, crevice corrosion and stress corrosion cracking, when low concentrations of contaminants, such as chlorides, are present. Therefore the choice of stainless steels as a canister external barrier is not recommended. The same considerations are also valid

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Table 1
Groundwater chemical composition

	NG (mg/l)	SG (mg/l)
Calcium	8.20	8.28
Magnesium	4.40	2.05
Sodium	95.00	80.20
Potassium	2.70	0.80
Carbonate	0	0
Bicarbonate	250.00	199.00
Sulfate	11.00	18.80
Chloride	21.00	14.50
Fluoride	2.30	0.39
Nitrate	5.10	0
Free carbon dioxide	2.00	0
Sulphide	0.25	0
Boron	0.08	0
pH	7.80	8.00

Non-detected: iron, manganese, arsenic, lithium, copper, lead, vanadium, zinc, phosphate, ammonium, nitrite and silicon. NG: natural groundwater; SG: synthetic groundwater.

for titanium. Even if this metal is more corrosion resistant than stainless steels, it is also susceptible to localized corrosion and hydrogen embrittlement [6].

In order to consider other alloys, less expensive and with better galvanic corrosion behavior in groundwater than the above mentioned alloys, tests on lead/SAE 1010 and lead/SAE 1020 carbon steels galvanic corrosion were carried out and reported in the present work.

2. Experimental

Galvanic corrosion tests were performed with high purity lead (99.99%), commercial lead (99.9%), SAE 1010 and SAE 1020 carbon steel. Carbon steel rectangular samples of 8 to 160 cm² and 1–2 mm thickness were used, according to test area ratios. Lead samples had an exposed

Table 2
Synthetic seawater composition

	g/l
Sodium chloride	24.53
Magnesium chloride	5.20
Sodium sulfate	4.09
Calcium chloride	1.16
Potassium chloride	0.69
Sodium bicarbonate	0.20
Potassium bromide	0.10
Boric acid	0.027
Strontium chloride	0.025
Sodium fluoride	0.003
pH	8.2

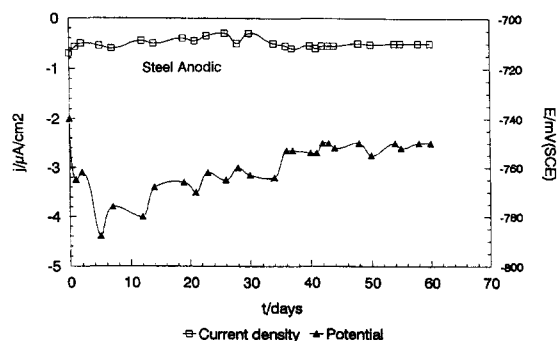


Fig. 1. High purity lead/SAE 1010 carbon steel galvanic test in 10% bentonite suspension/groundwater, 75°C, 1:10 area ratio.

area of 4 to 8 cm² and the same thickness as carbon steel samples. Lead samples were chemically polished according to NACE Standard TM-01-69 at room temperature before the tests, while carbon steel samples were polished with emery paper and pickled with sulfuric acid solution afterwards.

Electrode potential against a saturated calomel reference electrode and galvanic currents, with a zero resistance ammeter (ZRA), was measured every 24 h following ASTM Standard G 71-81. Tests were performed at 75, 50, 45 and 40°C in thermostated electrochemical cells.

The test solution was either synthetic groundwater with an approximate composition to the natural groundwater found at 500 m deep in the proposed repository site (Table 1), or synthetic seawater prepared according to ASTM Standard D 1141-75 (Table 2). Testing time was 60 days.

3. Results

Tests were performed for current density and electrode potential behavior in high purity and commercial lead/SAE 1010 carbon steel galvanic couples, and 1:10 area ratio in 10% bentonite suspension in synthetic groundwater at 75°C. In these tests, carbon steel behaved anodically up to

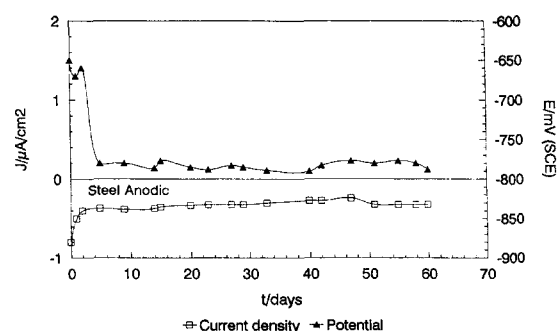


Fig. 2. Commercial lead/SAE 1010 carbon steel galvanic test in 10% bentonite suspension/groundwater, 75°C, 1:10 area ratio.



Fig. 3. SEM picture of commercial lead surface after galvanic test in 10% bentonite/groundwater, 75°C, 1:10 area ratio.

the end of the test, corroding preferentially (Figs. 1 and 2). Commercial lead presented some type of localized attack which was not detected in high purity lead, (Fig. 3).

The same type of tests with high purity and commercial lead/SAE 1010 carbon steel galvanic couples were also performed in synthetic groundwater without bentonite. A current polarity inversion occurred within 48 h of the beginning of the test, lead behaving then anodically up to the end of the test and corroding preferentially. This phenomenon was detected in all tests performed with this galvanic couple in synthetic groundwater at 75°C, and with different area ratios (Figs. 4 and 5).

Etching was detected in high purity as well as in commercial lead after the test (Fig. 6). Intergranular attack was also observed in commercial lead (Fig. 7). SAE 1010 carbon steel surface presented pitting, after testing in synthetic groundwater.

The effect of test temperature on high purity and commercial lead/SAE 1010 carbon steel galvanic couple behavior has also been checked. Tests were performed in synthetic groundwater, without bentonite, at 75°C during the first 30 days, and then for another 30 days at room

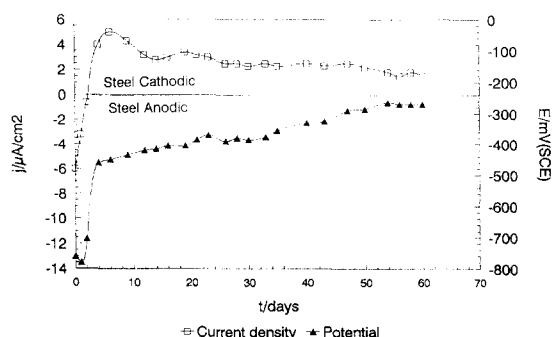


Fig. 4. High purity lead/SAE 1010 carbon steel galvanic test in groundwater, 75°C, 1:10 area ratio.

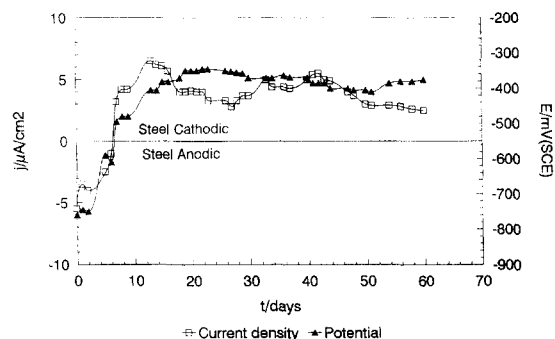


Fig. 5. Commercial lead/SAE 1010 carbon steel galvanic test in groundwater, 75°C, 1:10 area ratio.



Fig. 6. SEM picture of commercial lead surface after galvanic test in groundwater at 75°C, 1:10 area ratio.

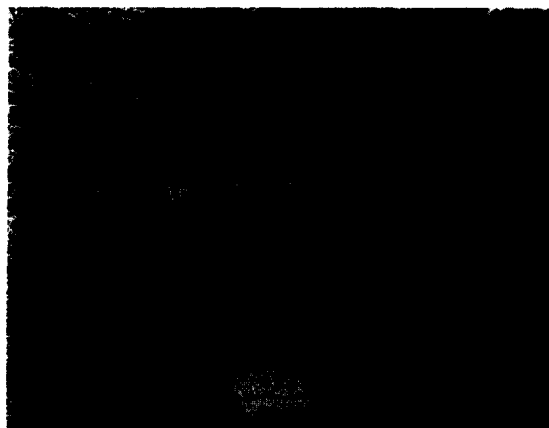


Fig. 7. SEM picture of commercial lead surface after galvanic test in groundwater at 75°C, 1:10 area ratio.

Table 3

Lead corrosion rates in commercial lead/SAE 1010 carbon steel galvanic tests in synthetic groundwater at 75°C

Galvanic couple	Area ratio	J ($\mu\text{A}/\text{cm}^2$)	Lead corrosion rate (mm/y)	
			galvanic current	weight loss
Pb	1	2.0	0.060	0.100
SAE 1010	10	–	–	0.070
Pb	1	1.9	0.057	0.056
SAE 1010	20	–	–	0.111
Pb	1	5.0	0.150	0.259
SAE 1010	40	–	–	0.114
Pb	1	5.1	0.150	0.180
SAE 1010	40	–	–	0.138

temperature. With a temperature decrease there is also a current density decrease with much lower lead corrosion rates.

Sixty day's galvanic corrosion tests on high purity lead/SAE 1010 carbon steel couples were also performed at room temperature, with the same area ratios and groundwater composition (with and without bentonite). In all tests, carbon steel behaved anodically up to the end of the test.

The influence of commercial lead/SAE 1010 carbon steel area ratio increase from 1:10 to 1:40 on lead corrosion rate, was tested in synthetic groundwater at 75°C. It was found that the area ratio does not affect the current polarity inversion phenomenon, and that lead corrosion rate is at least double when the area ratio increases from 1:10 to 1:40. Maximum measured commercial lead corrosion rate by weight loss was 0.259 mm/year (Table 3). For 1:40 area ratio, commercial lead presented a more pronounced intergranular attack than that found with 1:10 area ratio, Fig. 8.

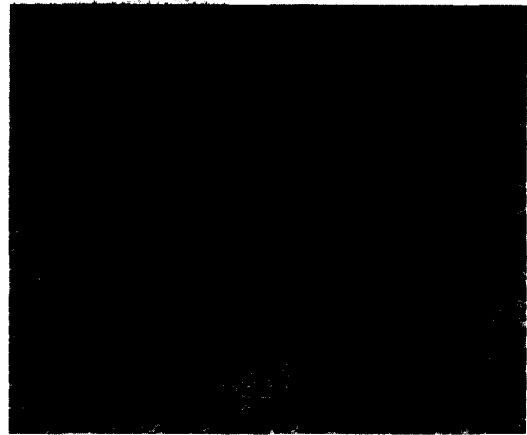


Fig. 8. SEM picture of commercial lead surface after galvanic test in groundwater at 75°C, 1:40 area ratio.

Carbon steel composition effect on galvanic corrosion behavior was also tested. Commercial lead/SAE 1020 carbon steel galvanic corrosion couples have been tested in synthetic groundwater, with and without bentonite at 75°C, with 1:10 area ratio. All tests showed a current density and electrode potential behavior similar to those found with commercial lead/SAE 1010 carbon steel in synthetic groundwater (Table 4). An increase of carbon content in steel has very little influence on the corrosion rate of steel in this galvanic couple.

In all tests performed with bentonite suspension in groundwater, lead behaved as a cathode with a very low corrosion rate (about 0.013 mm/year for commercial lead).

In order to determine the minimum temperature at which current polarity inversion is detected, commercial lead/SAE 1010 carbon steel galvanic corrosion tests were performed in synthetic groundwater at 50, 45, and 40°C. With a temperature decrease it was found that the time

Table 4

Commercial lead/SAE 1010–SAE 1020 galvanic corrosion rates in synthetic groundwater, 75°C, 1:10 area ratio

Media	Galvanic couple	J ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mm/y)	
			galvanic current	weight loss
Synthetic groundwater	Pb	4.3	0.129	0.123
	SAE 1010	–	0.042	0.168
	Pb	2.0	0.060	0.100
	SAE 1010	–	–	0.070
	Pb	2.8	0.084	0.140
	SAE 1020	–	–	0.154
	Pb	2.5	0.075	0.111
	SAE 1020	–	–	0.155
10% bentonite synthetic groundwater	Pb	–	–	0.011
	SAE 1020	5.6	0.006	0.057
	Pb	–	–	0.016
	SAE 1020	3.9	0.004	0.121

Table 5
High purity lead corrosion rate in different environments at 75°C

Environment	Corrosion rate (mm/y)
Natural groundwater (NG)	0.001
NG saturated with oxygen	0.007
Synthetic groundwater (SG)	0.003
10% bentonite suspension in distilled water	0.011
10% bentonite suspension in SG	0.007
NaCl 5×10^{-1} M solution	0.005
NaCl 5×10^{-3} M solution	0.024
NaCl 5×10^{-4} M solution	0.433
NaNO ₃ 1×10^{-1} M solution	0.493
NaCH ₃ -COO 1×10^1 M solution	0.664
Distilled water	0.565

elapsed for current polarity inversion increases. At 40°C, no current polarity inversion was detected at the end of the 60 day's test, lead behaving as a cathode up to the end of the test.

The effect of groundwater contamination with sea water on lead/SAE 1010 carbon steel galvanic corrosion behavior has also been studied, considering a seawater intrusion in the repository site due to an eventual geological change. High purity and commercial lead/SAE1010 carbon steel galvanic corrosion tests, 1:1 area ratio in 100, 50 and 25% synthetic seawater at 75°C were performed. In all cases no current inversion was detected, lead behaving cathodically up to the end of the test. Same type of tests were performed at 45 and 25°C, where no current polarity inversion was found.

4. Discussion

A higher lead corrosion rate was detected when high purity lead was galvanically coupled to carbon steel in synthetic groundwater at 75°C (about 0.1 mm/year), in comparison with uncoupled high purity lead corrosion rate, under the same testing conditions (0.003 mm/year) (Table 5) [1]. This higher corrosion rate is due to the current polarity inversion phenomenon that takes place few hours after the beginning of the test. This polarity inversion is due to the formation of a passivating film on the carbon steel surface, which then behaves as a noble metal, promoting the corrosion of lead. The ZRA current inversion may be induced by the cathodic reaction on lead (oxygen reduction) at the beginning of the test, which develops an alkaline pH on lead surface. This condition would promote the dissolution of protective lead oxides and basic salts. When a passive film is no longer present, lead will behave as an active metal (anode), and iron as a cathode. The cathodic reaction on iron will, in turn, induce a magnetite passivating film due to the increase of pH. Buffer proper-

ties of bentonite clay would prevent pH changes due to the cathodic reaction, and less protective iron oxide film such as hematite ($\gamma\text{Fe}_2\text{O}_3$), could develop [9].

Potential-time measurements in galvanic couples of carbon steel in groundwater at 75°C, showed that electrode potential increased to more noble potentials which, according to potential-pH diagram for iron, corresponds to the magnetite stability region [8]. Magnetite has been identified by X-ray spectroscopy on the steel surface after the test [5]. This phenomenon does not occur in groundwater at temperatures lower than 40°C. Magnetite passivating film formation is temperature dependent for this testing condition. This passivating film does not develop in 10% bentonite suspensions in groundwater at 75°C.

Higher corrosion rates and a grain boundary localized attack detected in commercial lead, galvanically coupled to carbon steel, are probably due to impurities present at the grain boundaries.

Discrepancies found between weight loss corrosion rates and calculated from ZRA galvanic current (Tables 3 and 4), may be due to localized corrosion cells inside pits or grain boundaries. It is well known that electrochemical conditions inside occluded cells are quite different from those at the metal surface. Another discrepancy is the steel weight loss when it behaves as a cathode. It should be considered that steel is anodic at the beginning of the test, and therefore it corrodes preferentially. On the other hand, the evolution of the galvanic potential through the test (-250 to -50 mV_{SHE}), is over the Fe/Fe²⁺ equilibrium potential, according to the potential-pH diagram for iron [8].

According to the literature, the grain size is a very important factor on the corrosion behavior of lead in soils and natural waters [10–13]. Larger grain size has a higher impurities concentration in grain boundaries than in a fine grain microstructure. Intergranular corrosion is due primarily to the segregation of impurities in grain boundaries [14].

Galvanic currents in dissimilar metals galvanically coupled depend, among other factors, on the area ratio. Larger cathodic areas (passivated carbon steel, for example) will provide more metallic surface for the cathodic reaction, therefore giving higher currents for the anodic dissolution in the smaller anodic area (lead), and hence higher corrosion rates. This will be the case if an eventual small failure occurs on the canister external carbon steel wall and, simultaneously, no bentonite shall be present at that time in the repository.

On the contrary, as the canister temperature decreases with time, the risk of this type of phenomenon also decreases. It was found an increase of the time elapsed for current polarity inversion with the decrease of temperature. At 40°C no polarity inversion was detected at the end of the 60 day's testing time, lead behaving as a cathode.

Increasing carbon content in steel (from 0.1 to 0.2%) has very little influence on its corrosion rate in groundwa-

ter, which actually is a mild corrosive media. Carbon steel corrosion rate values for synthetic seawater are much higher (0.2 mm/year) than those measured in synthetic groundwater (0.05 mm/year), for the same temperature and area ratio (75°C, 1:1). Iron does not passivate in seawater, therefore no current polarity inversion is detected.

The higher corrosivity of iron in oxygenated seawater is due to pitting corrosion. It is well known that, in this case, the corrosion potential matches the pitting potential of iron [7]. Usually there is no oxygen present in deep groundwater, but in case of an eventual oxygenated saline water intrusion, carbon steel corrosion rate will be very high.

The results of this study show that lead localized corrosion, induced by a galvanic pair, is the most dangerous situation for the proposed high activity nuclear waste canister integrity. According to the tests performed, commercial lead penetration rate for 1:40 area ratio and 75°C is, on average, 0.22 mm/year. This high corrosion rate is not compatible with the canister design life (about 1000 years). High purity lead coupled to carbon steel in groundwater at the same temperature, has a corrosion rate of about 0.1 mm/year, giving a much longer remanent life of the lead barrier.

It should also be pointed out that lead penetration rates were measured by weight loss, assuming a uniform corrosion process. In the case of commercial lead galvanic tests in ground water, intergranular corrosion was found. Hence, the real corrosion rate will be higher than that reported. Lead being a soft metal, intergranular corrosion penetration depth measurement by metallographic techniques is very difficult.

It should also be considered that the higher corrosion rates detected in lead were measured in groundwater with no bentonite clay present. This is one of the worst situations that could develop in the repository site. This condition could happen in a very long term, taking into account the very low water permeability of the rock.

In the eventuality of saline water intrusion in the repository, and according to the results of this study, carbon steel external liner will behave anodically, and therefore will corrode away, exposing the lead barrier to this aggressive environment. A lead corrosion penetration rate of 0.005 mm/year in 0.5 M NaCl solution at 75°C was found [5]. This chloride concentration is similar to that found in seawater. In the eventual case of seawater intrusion, the isolation of the high activity nuclear waste will be assured for periods longer than the design life. This low corrosion rate is due to the presence of a passive film of basic salts [16]. Archaeological studies also show that lead has a good corrosion resistance in seawater and in certain non-aggressive soils [10]. This corrosion resistance depends also on the microstructure and type of impurities present in the metal [12].

Therefore, a canister design with high purity lead as a

main barrier with a carbon steel liner, seems to be an acceptable choice for the long term isolation.

5. Conclusions

(1) Very low lead corrosion rates were found in lead/carbon steel galvanic couples in 10% bentonite suspension in groundwater tests at 75°C.

(2) Current polarity inversion was detected with lead/carbon steel galvanic couple in groundwater at 75°C, lead behaving as an anode and giving thus higher corrosion rates than in bentonite suspension.

(3) Commercial lead has higher corrosion rates than high purity lead.

(4) Commercial lead galvanic corrosion rate is at least double when the lead/carbon steel area ratio increases from 1:10 to 1:40, giving unacceptable corrosion rates.

(5) An increase of the carbon content of the steel has very little influence on steel corrosion rate in groundwater.

(6) Behavior of lead/carbon steel galvanic couple in seawater shows that there is no current polarity inversion and that there are higher steel corrosion rates than in groundwater. Lead behaved as a cathode down to the end of the test.

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