Kinetics, Thermodynamics and Mechanism of Lead Ion Removal in Presence of Surfactants

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Cementation of lead by zinc in lead nitrate solution was shown to be a feasible treatment process to achieve a high degree of lead removal over a broad operational range. The rate of lead removal was studied as a function of temperatures and the addition of certain surface active substance (SAS), at different concentrations of lead nitrate. The reaction of lead cementation was carried out with or without the anionic sodium dodecyl sulphate (SDS), the non-ionic Triton X-100 and the cationic cetyltrimethylammonium bromide (CTAB) which follows first-order reaction kinetics. Viscosity, percentage of inhibition and thermodynamic parameters ΔH^*, ΔS^* and ΔG^* were calculated and discussed. Cementation process was successfully applied to recover Pb^{2+} spiked to industrial wastewater sample.

Keywords: Kinetics, Thermodynamics, Viscosity, Cementation, Surfactants.

INTRODUCTION

Heavy metals or metalloids such as Hg, Cd, Pb and As are toxic to the cells at quite low concentrations[1]. Some metals as lead are discharged into environment in the form of organo-metallic species that can undergo further transformations[2-4]. The presence of metals in aquatic environment is known to cause severe damage to aquatic life because these metals kill micro organisms during biological treatment of wastewater with a consequent delay of water purification process[5,6].

Highly toxic metals, such as lead, tend to accumulate in bottom sediments from which they released by various processes of remobilization and in many cases they enter the food chain and are concentrated in fish and other edible organisms[7]. By reaching human beings, they produce chronic and acute ailments of various forms.

The cementation process has been demonstrated to be one of the successful methods for the removal of heavy metals from aqueous solutions. It is also one of the oldest and simplest hydrometallurgical processes which have been used as a means of extracting metals from solution. Only in the past twenty years, considerable attention has been paid to two main industrial applications of cementation. The first involves the recovery of metals from leach solutions[8] and the second is concerned with the purification of electrolyte solutions to remove metals which are more electropositive than the metal to be deposited, such as Cu, Co, Ni, Cd and as from $ZnSO_4$ electrolyte[9]. It has been reported that electrochemistry of the reaction at room temperature is diffusion controlled[10-16].

The objective of this work is devoted to study the kinetics, thermodynamics and mechanism of removal of Pb^{2+} on zinc rod in presence and absence of three surfactants at different concentrations and different temperatures.

EXPERIMENTAL

Kinetic measurements obtained by using a Beckman DB-G spectrophotometer (connected to a BAS X-Y recorder, which provides pens with maximum speeds of 2000 mm^{-1} s for the X-axis) and fitted with a cell housing maintained within ± 0.1 °C of the desired temperature.

Three different surfactants were used as received, sodium dodecyl sulphate as anionic surfactant, cetyltrimethylammonium bromide as cationic surfactant and Triton X-100 as anionic surfactant. The concentration of surfactants is in the range 10^{-5} to 10^{-3} mol L^{-1}. Five different concentrations of $Pb(NO_3)_2$ were used in which the zinc rod of 7 cm length and width 3.2 cm was immersed. The back side of the Zinc rod plate was insulated with polystyrene lacquer and the active surface of the zinc was polished with fine emery paper, degreased with trichloroethane, washed with alcohol and finally with distilled water.

Viscosity measurements were performed with an Ubbelohde viscometer. It was first clean with dilute chromic acid then rinsed with distilled water and finally with the solvent.

The viscometer with the solution was kept in a water thermostat for 0.5 h before measuring the flow time. The temperature was controlled within ± 0.01 °C.

RESULTS AND DISCUSSION

**Variation of rate constant on the cementation of lead:** The cementation reaction requires a transfer of electrons between the dissolving zinc and the precipitating lead. This requirement causes the lead to cement onto the zinc surface rather than remaining in the bulk of the solution. The kinetics of lead cementation have been reported extensively[13,16]. It is generally agreed that the rate-controlling step is the diffusion of lead ions onto the zinc surface. In such cases, the rate of change of lead concentration in the leach solution was monitored.
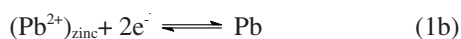
The overall cementation reaction is:

$$Pb(NO_3)_2 + Zn^0 \longrightarrow Pb^0 + Zn(NO_3)_2 \qquad (1)$$
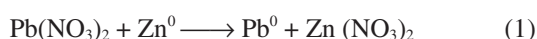
Mechanism of cementation reaction

Diffusion of the lead ions to the zinc or zinc lead metal surface:

$$(Pb^{2+})_{bulk} \longrightarrow (Pb^{2+})_{zinc} \qquad (1a)$$
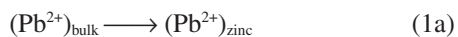
Transfer of electrons from the zinc to the lead:

$$(Pb^{2+})_{zinc} + 2e^- \rightleftharpoons Pb \qquad (1b)$$

The electrons participating in reaction (1b) are transferred from the zinc metal, where they are generated by the process:

$$Zn \rightleftharpoons Zn^{2+} + 2e^- \qquad (2a)$$
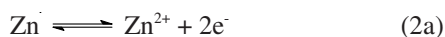
Diffusion of zinc ions from the metal surface to the bulk solution:

$$(Zn^{2+})_{Zn} \longrightarrow (Zn^{2+})_{bulk} \qquad (2b)$$

This reaction is diffusion-controlled and the rate in a batch reactor can be represented by eqn. 2:

$$\ln C_0/C = k\, A_t/V \qquad (3)$$

log C_0/C was plotted against time for different concentrations of lead nitrate and at different temperature as shown in Fig. 1. The values of rate constants represented in Table-1 show that the rate of mass transfer was increased by increasing concentration and temperature, *i.e.*, the cementation rate increases in the direction of precipitation of lead, indicating that the cementation reaction is a first-order reaction, as verified previously[12,13].
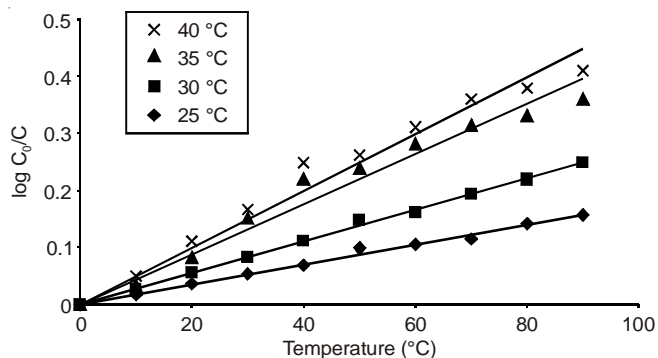

Fig. 1. Relationship between log C_0/C for blank solution at 50 ppm of Pb^{2+} solution and different temperature of $Pb(NO_3)_2$

TABLE-1
VALUES OF (k × 10⁴) AT DIFFERENT LEAD NITRATE CONCENTRATIONS AND DIFFERENT TEMPERATURES

Temp. (°C)	Pb(NO₃)₂ (ppm)				
	1	25	50	75	100
25	3.65	4.21	4.45	5.32	6.01
30	4.41	4.91	5.11	6.88	7.30
35	4.12	5.51	5.91	7.30	8.04
40	4.52	6.02	6.15	8.40	9.33

Diffusion of nitrate ions from the bulk solution into lead/zinc surface: The precipitated lead is deposited on Zn rod, thereby exhibiting two kinetic mechanisms[10,11]. The kinetic mechanism 2[17-19] operates when the lead ion diffusion rate is sufficiently slow that an appreciable degree of diffusion of nitrate ions (step 5) is allowed before the surface is substantially sealed off by the precipitated lead metal. The initial precipitation of lead is slowed significantly when the nitrate ions have time to diffuse into the pores of the precipitate, where the precipitant ion concentration and/or its hydrolysis products are high. In the pores, the nitrate ions will react by one of the several side reactions to produce several basic zinc compounds. It is possible that the formation of these basic compounds plays an important role in maintaining the progress of the cementation process. The basic nitrate grows in large flat platelets with large inter-layer spacing[20,21] and has demonstrated a propensity to incorporate foreign ions. Thus, growth of the crystals can open up the structure of the precipitate, allowing a relatively free inflow and outflow. The formation of basic zinc compounds will not cause passivation of the precipitant or cathodic lead, as ions can diffuse readily between the crystals and some possibly through the layers of the crystal structure.

It is concluded that the kinetics of present solutions obey this mechanism. At least in case of the Pb(NO₃)₂/zinc system, the cementation reaction was found to be a diffusion-controlled process whose rate can be calculated by plotting log C_0/C against time, t as shown in Fig. 2. For different lead nitrate concentrations at different temperatures, the data summarized in Fig. 2 indicate that the cementation reaction is a first-order reaction and this has been verified in previous work by other authors[17-19,22,23]. It is clear from Table-1 that the rate of mass transfer increased by increasing concentration and temperature, *i.e.* the cementation rate increases in the direction of precipitation of lead.
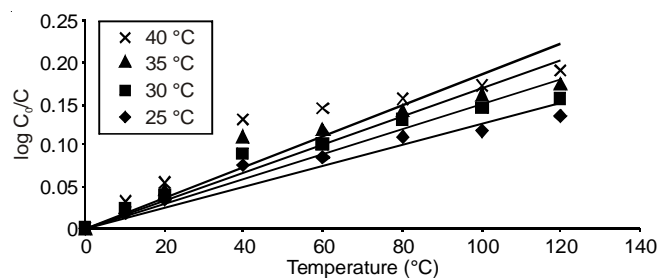

Fig. 2. Relationship between log C_0/C at 50 ppm of Pb^{2+} solution at different temperature of sodium dodecyl sulphate has concentration 5×10^{-5} mol L⁻¹

Effect of surfactants on the cementation reaction: The addition of a surface active substance (SAS) at different

concentrations decreased the rate of reaction (Table-2). This behaviour can be explained on basis that the viscosity of surface active substance-Pb(NO$_3$)$_2$ mixture is higher than that of Pb(NO$_3$)$_2$. Suppose k is the rate constant for a blank sample and k′ is the rate constant in presence of definite concentration of surface active substance, the relationship is described by the equation:

$$\text{Inhibition (\%)} = \left(\frac{k - k'}{k}\right) \times 100$$

TABLE-2
FIRST ORDER RATE CONSTANT (k × 10^4) FOR CEMENTATION OF Pb ON ZINC METAL PRESENCE OF SURFACE ACTIVE SUBSTANCE AT DIFFERENT TEMPERATURE

Temp. (°C)	Pb(NO$_3$)$_2$ (mol L^{-1})			
	1 × 10^{-5}	5 × 10^{-5}	10 × 10^{-5}	50 × 10^{-5}
Triton X-100				
25	3.61	2.81	2.28	2.26
30	4.36	3.53	2.89	2.71
35	4.65	5.25	4.43	3.66
40	4.92	5.78	4.89	4.31
ΔE* (KJ mol^{-1})	38.320	28.180	39.910	33.521
Cetyltrimethylammonium bromide				
25	1.85	1.38	0.831	0.641
30	2.02	1.49	1.202	0.624
35	2.20	1.60	1.380	0.736
40	2.88	2.21	1.823	0.928
ΔE* (KJ mol^{-1})	26.500	38.301	39.000	27.400
Sodium dodecyl sulphate				
25	1.68	1.12	0.801	0.502
30	1.82	1.40	1.005	0.808
35	1.92	1.53	1.12	0.93
40	2.02	2.02	1.80	9.01
ΔE* (KJ mol^{-1})	25.400	33.600	39.000	27.000

Table-3 shows that the % inhibition caused by surface active substance ranged from 20.2 to 81 %, dependent upon the type of surface active substance and its concentration, as well as on the bath temperature. Table-3 and Fig. 3 show the relationship between surfactant concentration and percentage inhibition.
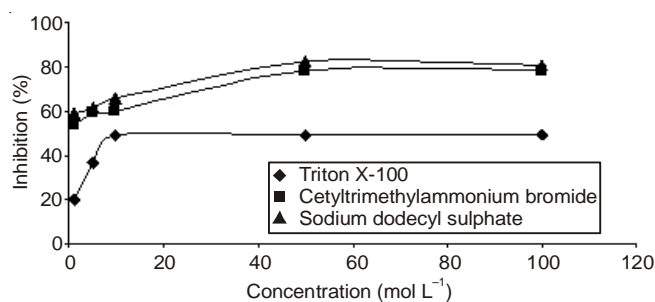

Fig. 3. Relationship between percentage inhibition and concentration for different surface active substance at 25 °C

The decrease in rate of cementation can be attributed to:

• Adsorption of surface active substance on the anode surface where it screens a part of anode, thus reducing the active anode area, with a consequential reduction in the rate of reaction[24,25].

• The adsorbed surface active substance increases the local solution viscosity at the anode surface, with consequence decrease[24] in the diffusivity of lead ions, which results in a decrease in the mass transfer coefficient k and in the limiting current, according to the following equation:

$$k = D/\delta \qquad (4)$$

where δ is the diffusion thickness, D is the diffusion coefficient and k mass transfer coefficient.

• The adsorbed substance molecules hinder natural convective flow arising from the density difference within the bulk solution and that at the electrode surface. This effect arises as a result of the fact that one end of organic molecules[25-30] is attracted to the electrode while the other end is attached to the solution.

Structural effect of surface active substance: It is found that the order of decreasing rate of reaction is as follows:

Anionic surface active substance (sodium dodecyl sulphate) > Cationic surface active substance (cetyltrimethylammonium bromide) > Non-ionic (Triton X-100)

This may be attributed to:

• Surface active substance may form a thin film on the metal surface, which tends to decrease the rate of cementation. In addition, adsorption of surface active substance on the zinc surface depends mainly on its structure. Although Triton X-100 has a longer hydrocarbon chain and sodium dodecyl sulphate has shorter one, the latter is adsorbed strongly on Zn metal. This is because sodium dodecyl sulphate has a negative charge, so it is attracted to the zinc surface so the amount of Zn dissolved is decreased and the rate of cementation is decreased.

• The decrease in the diffusion coefficient (D) of Pb^{2+} ion in solution containing surfactant is due to an increase in the interfacial viscosity, in accordance with the Stocks-Einstein equation:

$$D\eta/T = \text{constant} \qquad (5)$$

where T is the absolute temperature.

The increase in interfacial viscosity is caused by the adsorption of surfactant molecules at the metal surface with their polar ends directed towards the solution and the non-polar ends are directed towards the lead surface.

Mass transfer in presence of mixed surface active substance: The effect of binary mixture of surface active substance compounds has been studied in several cases. In

TABLE-3
RELATIONSHIP BETWEEN % INHIBITION (C × 10^5 mol L^{-1}) AND CONCENTRATION FOR ALL SURFACE ACTIVE SUBSTANCE AT 30 °C

	1 × 10^{-5} mol L^{-1}	5 × 10^{-5} mol L^{-1}	10 × 10^{-5} mol L^{-1}	50 × 10^{-5} mol L^{-1}	100 × 10^{-5} mol L^{-1}
Triton X-100	20.2	36.6	49.20	49.00	49.0
Cetyltrimethylammonium bromide	53.8	59.1	59.60	78.30	78.2
Sodium dodecyl sulphate	59.1	61.6	66.16	82.56	81.0

TABLE-4
EFFECT OF MIXED SURFACE ACTIVE SUBSTANCE ON THE RATE OF REMOVAL OF Pb^{2+} AT 25 °C

$C_{Sodium\ dodecyl\ sulphate}$ $\times 10^5$ mol L^{-1}	$C_{Cetyltrimethylammonium\ bromide}$ $\times 10^5$ mol L^{-1}	$k_{blank} \times 10^4$	K in presence of mixed surface active substance	Reduction (%)
1	1	5.35	1.62	70.28
	5		1.56	70.9
	10		1.48	72.38
	50		1.42	73.50
	100		1.38	74.25
5	1	5.35	1.43	73.32
	5		1.39	74.06
	10		1.30	75.74
	50		1.18	78.00
	100		1.10	79.50
10	1	5.35	1.40	73.58
	5		1.31	76.00
	10		1.20	77.61
	50		1.11	79.29
	100		1.08	79.85
$C_{Sodium\ dodecyl\ sulphate}$ $\times 10^5$ mol L^{-1}	$C_{Triton\ X-100}$ $\times 10^5$ mol L^{-1}	$k_{blank} \times 10^4$	K in presence of mixed surface active substance	Reduction (%)
1	1	5.35	1.98	63.6
	5		1.84	65.65
	10		1.74	67.53
	50		1.68	68.65
	100		1.60	70.14
5	1	5.35	1.82	66.0
	5		1.70	68.28
	10		1.65	69.21
	50		1.54	71.26
	100		1.48	72.35
10	1	5.35	1.72	67.91
	5		1.68	68.65
	10		1.60	70.14
	50		1.51	71.81
	100		1.41	73.60

many industrial applications, surface active substance are invariably mixtures as they are produced from feedstocks containing mixed hydrocarbon chain lengths. The surfactants used in practical applications are usually mixtures of surface active substance. This may be due to (i) The cost of producing pure substances is very high. (ii) • The fact that, in many practical applications, the surface active substance mixture has much better properties than those of the individual components.

Rate of cementation in presence of anionic-cationic surface active substance: The addition of cetyltrimethylammonium bromide as (cationic surface active substance) to sodium dodecyl sulphate (anionic surface active substance) greatly increases adsorption (Table-4). The superiority in performance for mixtures of similar or dissimilar surface active substance is attributed largely to synergistic behaviour among the molecule mixtures[21]. In this case, the expected micelle will be formed from two head groups and a double chain of surfactants. The mixed surface active substance exhibits a large synergistic surface tension reduction and mixed adsorption films are formed which are more inhibitive[21] to the rate of cementation.

Rate of cementation in presence of non-ionic + anionic surface active substance: In presence of Triton X-100 (non-ionic surface active substance) and sodium dodecyl sulphate (anionic surface active substance) or cetyltrimethylammonium

bromide (cationic surface active substance) the percentage inhibition is larger than Triton X-100 alone, as shown in Table-4, due to dipole charge interaction[21,22].

Thermodynamic treatment of the results: The activation energy of the process is an important parameter for determining the rate-controlling step. If boundary layer diffusion of the aqueous species is the rate controlling step[21], E is generally $\leq$ 28 Kj mol^{-1}, whereas if adsorption of the species on the reaction surface and subsequent chemical reaction take place, the E values are usually > 43 Kj mol^{-1}.

The values of E for all of the different solutions are given in Table-5. It is obvious that E < 27Kj mol^{-1}. This indicates that the cementation reaction in the presence and absence of surface active substance is controlled by diffusion processes.

The activation energy of the reaction E was obtained from Arrhenius equation:

$$\ln k = -E/RT + \ln A \qquad (6)$$

where R is the gas constant [8.314 k J^{-1} mol^{-1}]: E is the activation energy and A is the frequency factor. The values of E were used to calculate enthalpy of activation ΔH^*, entropy of activation ΔS^* and free energy of activation ΔG^* using the following equations:

$$\Delta H^* = E - RT \qquad (7)$$
$$\Delta S^*/R = \ln A - \ln B\ T\ e/h \qquad (8)$$
$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (9)$$

TABLE-5
THERMODYNAMIC PARAMETER OF DIFFERENT
SURFACE ACTIVE SUBSTANCE AT 25 °C

$C \times 10^5$ mol L^{-1}	ΔG^* (KJ mol^{-1})	ΔH^* (KJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
Blank			
1	92.73 ± 6.72	37.42 ± 3.40	185.53 ± 11.10
5	93.2 ± 9.60	35.34 ± 4.80	194 ± 15.96
10	93.85 ± 9.20	36.27 ± 4.66	193 ± 15.00
50	93.2 ± 6.85	42.75 ± 3.47	171 ± 11.30
Triton X-100			
1	90.677 ± 3.20	35.843 ± 3.4	185.2 ± 10.2
5	79.342 ± 4.20	25.70 ± 4.8	190 ± 9.30
10	94.35 ± 5.12	37.4 ± 4.3	191 ± 12.2
50	87.96 ± 5.10	31.04 ± 3.2	182 ± 10.0
Cetyltrimethylammonium bromide			
1	96.137 ± 3.80	24.02 ± 0.66	242 ± 2.19
5	105.6 ± 10.2	35.841 ± 2.16	235 ± 9.50
10	105.6 ± 8.12	36.52 ± 1.21	230 ± 1.67
50	97.693 ± 6.12	24.981 ± 40.0	244 ± 1.15
Sodium dodecyl sulphate			
1	95.952 ± 1.66	22.92 ± 0.66	235 ± 2.21
5	99.652 ± 3.68	31.118 ± 1.86	230 ± 3.12
10	103.57 ± 2.89	36.521 ± 2.52	225 ± 2.16
50	96.441 ± 5.30	24.921 ± 4.03	240 ± 3.15

where B is the Boltzman constant, e is 2.7183, h is Plank's constant.

The increase in the heat of adsorption leads to an increase in the energy of adsorption forces. However, raising the temperature acts in the reverse direction, increasing the kinetic energy of the molecules, facilitating the rate of adsorption (and consequently in physical adsorption). In absence of surface active substance, the activation energy = 25 kJ mol^{-1}, which is smaller than when surface active substance is used as inhibitor. Thus, the high values of activation energies show that:

• The rate of lead cementation is increased by addition of surface active substance at temperatures above 20 °C.

• The adsorption process is a physical adsorption[17].

Conclusions

• The rate of the Pb(II)/Zn cementation reaction in the presence of surfactants as non-ionic (Triton X-100), anionic (sodium dodecyl sulphate) and cationic (cetyltrimethylammonium bromide) substances was lower than that in a blank solution (*i.e.* lead nitrate solution). The ranking order of the decreasing rate was Triton X-100 > cetyltrimethylammonium bromide > sodium dodecyl sulphate.

• The rate of cementation was increased by temperature and the reaction is a diffusion-controlled process.

The presence of two different surfactant compounds in the solution was more effective than that in the presence of only one.

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