ISSN 0-0354 111
Bull. Nat. Inst. Of Oceanogr. & Fish., A.R.E., 2000. Vol. (26): 257 - 269

APPLICATION OF CEMENTATION ON INDUSTRIAL WASTE WATER

BY

MAHMOUD, TH. H.*; EL SUBRUITI,G.M.; EL SHAZLY, SH. A. AND SHALTOUT, N. A.

* *National Institute of Oceanography and Fisheries.*

Key Words: Cementation process, Industrial waste.

ABSTRACT

Industrial waste water samples were collected from the drains of two factories, Egyptian Company for Plastic Industries and Batteries Production and El-Beda Dyers Company. The waste water quality were determined. Cementation reactions were followed on filtered samples under reaction conditions 700 rpm, 40 °C, 7 hour reaction period and exposed surface area of Zn cylinder were 47.13 cm^2, 49.76 cm^2 for the two samples of the two stations respectively. Cementation reaction rate of Cu^{+2} and Pb^{+2} in each sample were estimated where, 94.5% of copper and 96.5% of lead were recovered from the waste water of the Egyptian Company for Plastics Industries and Batteries Production and 88.7% of copper and 82% of lead were recovered from El-Beda Dyers Company.

INTRODUCTION

Cementation is used as a general term to describe the process whereby a metal is precipitated from a solution of its salts by another more electropositive metal. Such reactions have been and are being, used extensively in the minerals industry, both for the recovery of values (e.g. the extraction of copper from leach streams with iron [Rickard, and

Fuerstenau 1968] or gold recovery from cyanide leach solution [Nicol, ***et al.***, 1979] also for copper recovery from cyanid liquors [Hsu, ***et al.***, 1998; Kakovskii., ***et al.***, 1967]) and for the purification of process streams (e.g. the removal and recovery of copper and cadmium from zinc sulfate electrolyte with metallic Zn). The metal used need not to be of highest purity. On the other hand, when metals such as copper are treated they are converted into essentially pure metal powders so that cementation is one of the most effective and economic techniques for recovering toxic and/or valuable metals from industrial waste solution [Shcherbakov and Kakovskii 1967; Lo, and Yu, 1992; Guerra and Dreisinger, 1999]. All authors have reported that the cementation reactions take place under diffusion controlled mechanism at room temperature [Ravindea and Milton, 1967; Strickland and Lawson, 1970, Maklufi, ***et al.***, 1997, Makhloufi, ***et al.***, 1998, Mishra and Paramguru, 1999, Shaltout 1999, Joon, ***et al.***, 2000, Nosier and Sallam 2000, Ismail, ***et al.***, 2001].

Industrial waste water samples were collected from the drains of two factories, Egyptian Company for Plastic Industries and Batteries Production and El-Beda Dyers Company. These industries discharge their wastes into Abu keir drain, which in turn disposed off its water into the sea at Abu-keir bay, via El-Tabia pumping station causes pollution of the bay and affect the aquatic environment and fishes.

The aim of this work is to estimate the heavy metals Cu^{+2} and Pb^{+2} concentrations and estimates the efficiency of cementation reaction method as a treatment method for removing heavy metals from industrial waste water electrochemically without using any external chemicals. Water quality of the collected industrial waste water samples from the two factories was also measured.

MATERIALS AND METHODS

Waste water samples were collected from the drains of Egyptian Company for Plastic Industries and Batteries production and El- Beda Dyers Company. The water quality of these samples was measured. pH, was determined immediately after collection using a portable glass electrode pH meter (type: water test, HANAA instrument, Italy) accurate to 0.1 pH.

carbonate and bicarbonate, both were determined immediately after collection of the samples volumetrically according to (APHA, 1981) using phenolphthalein and methyl orange indicators, and standard 0.02 N H_2SO_4 , chlorsity, was determined according to Mohr's Method (APHA, 1981), suspended matter was determined gravimetrically according to (APHA, 1981), organic matter was determined by back titration using 0.01 N $Na_2S_2O_3$ standard and starch indicator according to (APHA, 1981). Determination of inorganic phosphate with an acidified molybdate reagent to yield a phosphomolybdate complex, which is then reduced to a colored blue compound the method used in this study was described by (Grassoff,1976). The determined heavy metals Cu, Pb, Cd, Ni, Cr, Zn, Fe, Mn, were preconcentrated using digestion with concentrated nitric acid according to standard method (APHA, 1981) and then their concentration were measured using flame Atomic Absorption Spectroscopy.

The cementation method for industrial waste water treatment was applied to these collected samples in order to decrease concentrations of copper and lead and other existed heavy metals in both samples. The block diagram of the apparatus that was used in this method as shown in Figure (1) which permits the rotation of clamping Zinc cylinder assembly arranged such that only the peripheral surface of pure Zinc was put in one liter vessel solution. The cylinder was rotated in experimental solution with variable speed motor. The frequency of rotation recorded as revolution per second was counted by an optical tachometer. The reaction vessel was set in a constant ± 0.05 ultratheromostat.

RESULTS AND DISCUSSIONS

Samples from two different water areas were collected, Egyptian Company for Plastic Industries and Batteries production and El Beda Dyers Company.

1-Egyptian Company for Plastic Industries and Batteries Production :

There are two main industries in this company, plastic industries and batteries production. The production of batteries requires the use of lead for the plates used within the batteries, the plates may be either newly made or produced from used batteries. The wastes were generated in the

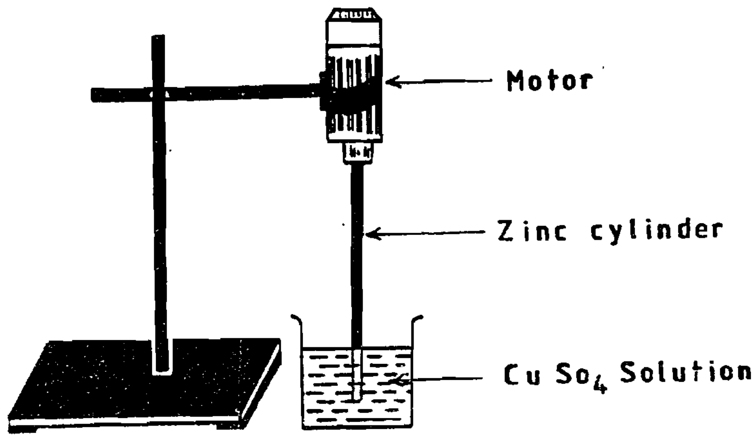

Fig. (1): Diagram of apparatus used in cementation reaction.

plate forming areas and where the batteries were cleaned and filled. Wastes were acidic, highly corrosive due to the use of sulfuric acid, highly turbid and rich in heavy metals especially Pb as $PbSO_4$ in the ionic form. Sampling was chosen to be a representative for the partially treated waste water of batteries production unit.

Water characteristics of collected samples were measured and illustrated in Table (1-a, b). It was found that pH and alkalinity values were very low with an average of 1.55 and 72.96 mg CO_3^{-2} l^{-1} respectively. This is attributed to the use of high quantity of H_2SO_4 in batteries production for washing lead plates and for batteries cleaning and filling. It was also found that suspended and organic matter content were high with an average of 11.82 g l^{-1} and 10.63 mgO_2 l^{-1} respectively. Chlorosity was recorded as 137.13 mg Cl^- l^{-1} and low value of phosphate 0.13μgmoll^{-1} was also recorded. Heavy metals concentrations values were 2.46 ppm, 7.53 ppm, 0.07 ppm, 1.62 ppm, 0.02 ppm, 0.003 ppm, 0.02 ppm and 0.01 for Cu, Pb, Zn, Fe, Mn, Cd, Cr and Ni respectively.

Table (1): Water characteristics of samples of industrial waste water from

Station 1: Egyptian Company for Plastics Industries and Batteries production
Station 2: El-Beda Dyers Company

a) Water quality of station (1) and station (2)

Station	pH	Alkalinity $mgCO_3\ l^{-1}$	Suspended matter $g\ l^{-1}$	Organic matter $mgO_2\ l^{-1}$	Chlorosity $mg\ Cl^-\ l^{-1}$	Phosphate μg at p l^{-1}
1	1.55	72.96	11.82	10.63	137.13	0.13
2	11.38	556.50	0.57	16.79	583.80	33.56

b) Heavy metal ions concentrations (ppm) in station (1) and station (2)

Station	Cu^{+2}	Pb^{+2}	Zn^{+2}	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cr^{+3}	Ni^{+2}
1	2.46	7.53	0.07	1.62	0.02	0.003	0.02	0.01
2	2.04	2.45	0.08	0.51	0.01	0.001	0.12	0.05

Cementation reactions were followed on filtered sample that contained 2.456 ppm Cu^{-2} and 7.530 ppm Pb^{-2}. Data were represented in table (2) and graphically in figure (2). The cementation reaction rates of Cu^{-2} and Pb^{-2} were estimated from the relation between log Co/C for Cu^{-2} or Pb^{-2} with time as shown in figures (3,4) according to the equation log Co/C = KA/V 2.303

Where A: exposed zinc surface area (Cm^2)
V: The volume of the solution recovered (ml).
Co: intional Cu^{-2} or Pb^{-2} concentration (ppm).
C: Cu^{-2} or Pb^{-2} concentration at time t (ppm).
K: mass transfer coefficient.

The concentrations of Cr, Cd and Ni ions at the end of cementation reaction were measured, while other metal Zn and Fe would not participate in this reaction. The reason for Zn is that the used rode was made from Zn metal and for Fe is that Fe metal is before Zn metal in the electrochemical series. The reaction conditions were 700 rpm, 40°C and 7 hour reaction period. The exposed surface area of Zn cylinder was 47.13 cm^2.

Applying cementation reaction decreased Cu^{-2} and Pb^{+2} concentrations gradually. After 1 hour, the Cu^{+2} and Pb^{-2} concentration in reacting solution would be 1.64 ppm and 4.69 ppm respectively i.e. Cu^{+2} concentration decreased by 33% and Pb^{-2} concentration by 37.6% while after 2 hour they became 1.072 ppm and 2.830 ppm respectively, then after 4 hour they were found to be 0.437 ppm Cu^{-2} and 1.127 ppm Pb^{-2}, i.e. about 82% of initial Cu^{-2} concentrations and 85% of initial Pb^{-2} concentrations are recovered. As shown from table (2) at the end of the experiment it was found 0.138 ppm and 0.283 ppm for Cu^{-2} and Pb^{-2} respectively i.e. about **94.5% Cu^{+2}** and **96.5% Pb^{+2}** are recovered from the waste water drains of batteries Company. These results from invironmental impact could be considered satisfied because the remaining heavy metals concentrations were present in trace amount when they were diluted more and more before dumped to the aquatic environment. The cementation reaction rate for each Cu^{-2} and Pb^{-2} were estimated and the mass transfer coefficient is then calculated from Fig. (3,4) this was found to be $\mathbf{K_{Cu} = 2.443 \times 10^{-3}\ sec^{-1}}$ and K_{Pb} $\mathbf{= 2.852 \times 10^{-3}\ sec.^{-1}}$

Table (2): The percentage recovered of Cu^{+2} and Pb^{+2} through cementation reaction within time for sample from station (1).

Cu^{+2}			Pb^{+2}		
Time Min.	**Conc. Ppm**	**% Cu^{+2} recovered**	**Time min.**	**Conc. ppm**	**% Pb^{+2} recovered**
Zero	2.456	Zero	Zero	7.530	Zero
60	1.642	33.0	60	4.696	37.6
120	1.072	56.4	120	2.830	62.4
180	0.777	68.4	180	1.786	76.3
240	0.437	82.0	240	1.127	85.0
300	0.309	87.4	300	0.671	91.1
360	0.184	92.5	360	0.414	94.5
420	0.138	94.5	420	0.283	96.5

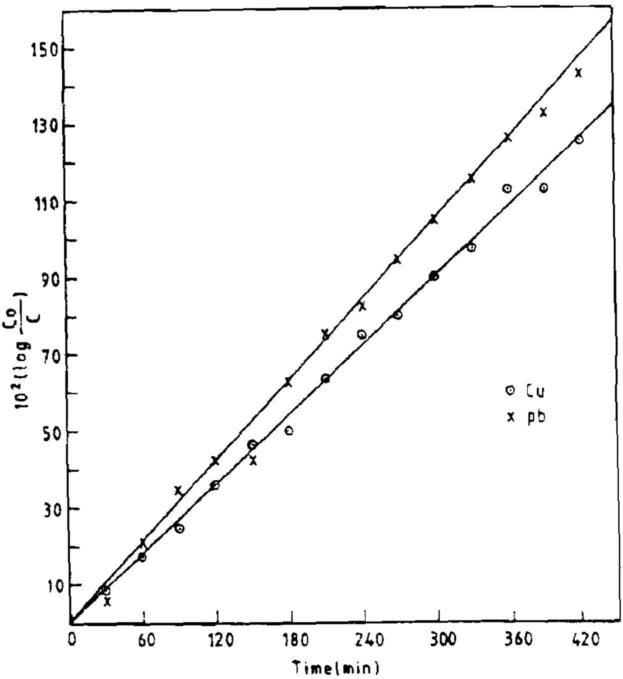

Fig. (2): The relation between log Co/C and time for Cu^{++} and Pb^{+-} in sample from station I at 40°C and rpm = 700

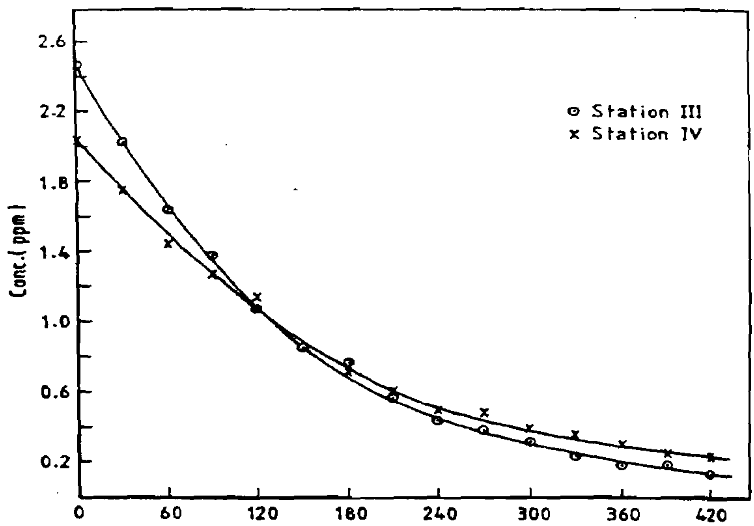

Fig. (3): The relation between the concentration and time for Cu^{++} in samples from station I and station II

On the other hand other heavy metals present in the reacting solution Cr, Ni and Cd were also cemented on Zn cylinder during reaction because they are more electronegative than Zinc. It was found that their concentration at the end of the experiment were reduced to 0.008 ppm for Cr i.e about 60% of initial Cr was extracted, 0.009 ppm for Ni i.e about 10 % of initial Ni was extracted and 0.001 ppm for Cd i.e about 33.3% of initial Cd was extracted.

2- El-Beida Dyers Company:

It is considered as one of the largest industries for cotton textile finishing, and wool textile production in the middle east. The plant produces about 143 million meter of dyed and printed yarns and fabrics, as well as 600 ton of scoured and sypum wool yarn, about 1500 ton of this amount are dyed. The plant is divided into three factories, cotton finishing factory, wool textile production factory and the synthetic fibers factory. Sample was chosen to be a representative for mixed wastes of final partially treated waste water effluent resulting from the primary finishing process including (desizing, scouring bleaching, and souring steps of the fabric) with the waste water from dyeing and printing processes, also with the alkaline wastes from the sodium hydroxide recovery unite. Dying process is a main source for highly metal concentration in the discharged waste water, its wastes might contain metals such as Pb, Cu, Fe, Cr, Co, Ni.

Waste water characteristics are given in Table (1, a-b). High pH value of the waste water 11.38, could be attributed to two reasons a) the alkaline wastes from the sodium hydroxide recovery unite and b) using of alkaline NaOH solution in primary finishing process unite, so alkalinity is found to be very high 556.50 mg CO_3^{-2} l^{-1}. Chlorosity showed values of 583.80 mgCl^- l^{-1}, oxidizable organic matter was found to be 16.79 mgO_2 l^{-1}, and small amount suspended matter 0.57 gl^{-1} was determined. The high content of inorganic phosphate 33.56 μgmoll^{-1}, may be caused by two factors; the first is the removal of dissolved oxygen by active decomposition of organic matter which release the soluble phosphate and the second may be attributed to the fact that dye contain phosphorous compounds causing this very high value.

Heavy metal concentrations in the discharged waste water of El-Beida Dyers Company were found to be 2.04ppm Cu^{-2}, 2.45ppm Pb, 0.08ppm Zn, 0.51ppm iron, 0.01ppm Mn, 0.001ppm Cd, 0.12ppm Cr and 0.05ppm Ni..

Cementation reaction is applied on filtered sample that contains 2.04 ppm Cu^{-2} and 2.45 ppm Pb^{-2}. The cementation reaction rates of Cu^{-2} and Pb^{-2} is estimated and the concentrations of Cr, Cd and Ni at the end of cementation reaction were measured. The reaction conditions were 700 rpm, 40°C and 7 hour reaction period. The exposed surface area of Zn cylinder were 47.13 cm^2.

By following cementation reaction on the filtered sample the gradual decrease in Cu^{2-} and Pb^{2-} concentrations with the time is represented in table (3) and Fig. (5). After 1 hour the concentrations decreased by 29.2% and 20.5% for Cu^{2-} and Pb^{-2} respectively and after 4 hour the recovery of Cu^{-2} and Pb^{-2} were recorded to be 76.3% and 62.4%, while at the end of the reaction they become 0.229 ppm and 0.359 ppm i.e. **88.7%** of initial Cu^{-2} concentration and **82%** of initial Pb^{-2} concentration are completely recovered at the end of the experiment as shown in Table (3). Mass transfer coefficient was found to be $\mathbf{K_{Cu} = 1.882 \times 10^{-3}\ sec^{-1}}$ and $\mathbf{K_{Pb} = 1.362 \times 10^{-3}\ sec^{-1}}$ as indicated from Figs . (3 & 4) which represented the relation between log Co/C for Cu^{-2} and Pb^{2} against time.

It was also noticed that Cr, Ni metal ions concentrations were reduced at the end of experiment up to 0,098 i.e about 18.3% of initial Cr was extracted and 0.034 i.e about 32% of initial Cr was extracted, while Cd metal concentration may be completely treated since there was no any evident for any Cd present.

It was observed that the cementation reaction rate of copper in filtered sample from Egyptian Company for Plastics Industries and Batteries Production were higher than that from El-Beda Dyers Company although both of them have the same initial Cu^{-2} contained is may be attributed to the difference in pH values since sample from Egyptian Company for Plastic Industries and Batteries Production is highly acidic (pH=1.55) while sample from El-Beda Dyers Company is highly alkaline (pH=11.38) [Hanaa, 1998] since Cu^{-2} removals by cementation reaction increases by decreasing pH.

Table (3): The percentage recovered of Cu^{+2} and Pb^{+2} through cementation reaction within time for sample from station (2).

Cu^{+2}			Pb^{+2}		
Time min.	**Conc. ppm**	**% Cu^{+2} recovered**	**Time min.**	**Conc. Ppm**	**% Pb^{+2} recovered**
Zero	2.037	Zero	Zero	2.45	Zero
60	1.442	29.2	60	1.946	20.5
120	1.145	43.8	120	1.571	35.9
180	0.765	62.4	180	1.057	57.0
240	0.483	76.3	240	0.921	62.4
300	0.33	83.8	300	0.691	71.8
360	0.304	85.1	360	0.615	74.9
420	0.229	88.7	420	0.441	82.0

It could be concluded that, cementation process could be applied to the industrial waste water before discharging to the marine environment either in the factories treatment units or in the waste water treatment plant (such as El-Tabia Pumping station). It can be also concluded that more better, efficient and faster results for complete recovery of heavy metals that are more electronegative than Zn could be obtained by applying more rotational speed of Zinc cylinder, larger exposed Zinc surface area, lowering pH value and raising temperature up to 40° C.

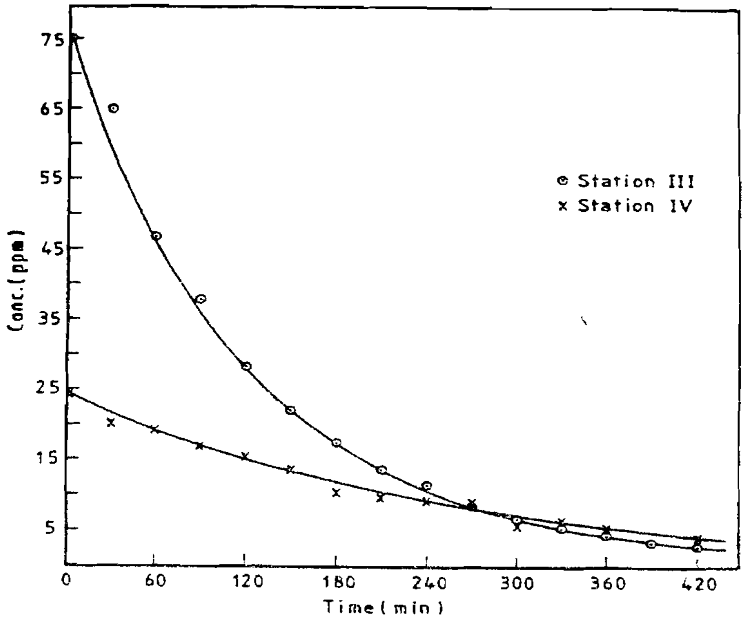

Fig. (4): The relation between the concentration and time for Pb^{++} in samples from station I and station II.

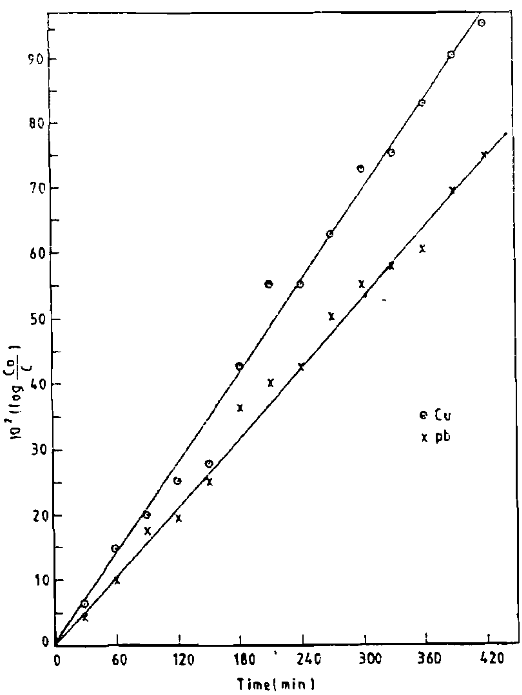

Fig. (5): The relation between the concentration and time for Pb^{++} in samples from station I and station II.

REFFERENCES

APHA, 1981. Standard Methods for the Examination of Water and Waste Water, American Public Health Association, American Water Works Association and Water Pollution Control Federation, New York pp. 769.

Grassoff, R., 1976. Methods of Sea Water Analysis, New York, pp. 137.

Guerra, E.; Dreisinger, D. B.; 1999, A study of factors affecting copper cementation of gold from ammoniacal thiosulfate solution, Hydrometallurgy, 51,(2), 155.

Hanaa H. Abd El- Rhman, 1998. Studies of Cementation of Copper on Rotating Zinc Cylinder in Aqueous and Mixed Solvents, Ph. D. Thesis Submitted for Faculty of Science, Alexandria University, Egypt, 220.

Hsu, Y. J.; Kim, M. J; Tran, T., 1998. Electrochemical study on copper cementation for cyanide liquors using zinc, Electrochemical Acta 44, 1617.

Ismail; A. M.; Elnagar, G. A. and Ahmad, A. M.; 2001. Production of copper powder on rotating iron cylinder, Bullatin of electrochemistry, 17,(10), 520.

Joon- Ho Shin, Ki- Won Kim and Hyo- Jun Ahn, 2000. Preparation from lead acid battery cementation reaction, Journal Of Power Sources, 89,(1), 46.

Kakovskii, I. A; Shcherbokov, O. K.; 1967. Kinetics of noble metal cementation from cyanide solution, Izv: Akad. Nauk. S.S.S.R., Metally, 1, 79.

Lo, K. S. L; Yu, Y. H.; 1992. Removal of soluble silver ion by cementation processes, Water Treatment 7, 127.

Maklufi. L.. Saidani. Bb. and Dimanova. L. 1996. Kinetics f copper cementation by lead in sulfate medium. Izv Vyssh. Uchebn. Zaved. Chem. Metall.. 5. 7.

Maklufi, L.: Saidani. Bb.: and Cachet. C. and Wiart, R.: 1998. Cementation of Ni^{+2} ions from acidic sulfate solution onto a rotating zinc disc, Electrochemical Acta. 43. (21-22). 3159.

Mishra, K. G, Paramguru, R. K., 1999. Studies on cementation of copper from sulphate solutions onto zinc metal. Trans. Indian. Inst. Met., 52,(2-3), 109.

Nicol,M. J., et al., 1979, A modern study of the kinetics and mechanism of the cementation of gold. J. of the South African Inst. of Minerals and Metallurgy, 79. 191.

Nosier: A.. Sallam, S. A., 2000. Removal of lead ions from waste water by cementation on a gas-sparged zinc cylinder. Separation and Purification Technology. 18. (2). 93.

Ravindea M. Nadkarni. Milton E. Wadsworth. 1967, A kinetic study of copper precipitation on iron. Transactions of the Metallurgical Society of Aim, 239, 1066.

Rickard, R. S., Fuerstenau, M. C., 1968. An electrochemical investigation of copper cementation by iron, Transactions of the metallurgical society of aim, 242, 1478.

Shaltout, N. A, 1999. Kinetic study of cementatin reactin of heavy metals on industrial waste water. MSC these. Chemistry department, Faculty of science. Alexandria University. pp199

Shcherbakov, O. K. and Kakovskii, I. A. 1967 Kinetics of coprecipiattion of gold, silver, and copper from cyanide solutions, Tsvet. Metally, 40 (2), 10.

Strickland, P. H., Lawson, F.. 1970. Cementation of copper with zinc from dilute aqueous solutions Proc. Aust. Inst. Met. 236, 25.