PRJ, Vol. 6 (January 1994); P. 91–95, 1 FIG, 3 TABLES.

Short Note

EFFECT OF THE GRAVITY SEDIMENTATION AND CHEMICAL PRECIPITATION ON THE CONCENTRATION OF HEAVY METALS IN THE REFINERY EFFLUENT

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تأثير التراكم التثاقلي والترسب الكيميائي على تركيز المعادن الثقيلة في منصرف معامل التكرير

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تم تقدير تركيز المعادن الثقيلة في منصرف معامل التكرير بواسطة جهاز طيف الإمتصاص الذري. كما إختبرت معملياً بعض المخثرات الكيميائية — مثل أكسيد الكالسيوم وحامض الكبريتيك وكبريتات الألومنيوم المائية — لدراسة كفاءتها على الحد من تركيز المعادن الثقيلة في المنصرف المعنى. وجد أن إضافة أكسيد الكالسيوم أو كبريتات الألومنيوم المائية بتركيز 500 جزئ/المليون ثم ترك عينات المنصرف لمدة 24 ساعة للسماح بترسب المادة المخثرة ، قد أدى إلى خفض تركيز المعادن الثقيلة بنسبة أكبر من التراكم التثاقلي على حدى. إضافة حامض الكبريتيك أدى إلى خفض تركيز الحديد والكروم والنحاس ، بينما كان التأثير معاكس بالنسبة للنيكل والخارصين والرصاص.

INTRODUCTION

Some of the heavy metals are among the list of harmful elemental substances, such as iron, chromium, copper, nickel, lead and zinc. These elements can be found in the industrial discharge, such as refinery effluent.

Our study mainly concentrates in locating suitable, easily available and economical precipitating agents and determining their optimal concentration in which they can be used to achieve the maximum efficiency, regarding the reduction of percentage concentration of metallic constituents in the refinery effluents or in other industrial discharges.

Concentration of heavy metals in the refinery effluent were estimated by using Atomic Absorbtion Spectrometric Technique. Some known chemical coagulants were tested to estimate their efficiency for reduction the heavy metals level in the effluent. These are calcium oxide, sulphuric acid and aluminium sulphate octadecahydrate. It was found that the calcium oxide or hydrated aluminium sulphate, when added in the refinery effluent, in the concentration of 500 ppm as coagulant and simultaneous sedimentation for a period of 24 hours, reduced the percentage concentration of the contained heavy metals more than the reduction caused by the sedimentation alone. In case of sulphuric acid, reduction in concentration of iron, chromium and copper have been obtained while it has an opposite effect with nickel, zinc and lead metals. All experiments were carried out at laboratory scale.

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EXPERIMENTAL WORK

(a) Reagents and Materials

(i) Purity of reagents; the following chemicals of the ACS grade conforming to specifications of the Committee on Analytical Reagents of the American Chemical Society were used: concentrated hydrochloric acid, concentrated nitric acid, concentrated perchloric acid, concentrated ammonium hydroxide

(contains 30% ammonia), 8-hydroxyquinoline, diphenylthiocarbazone, methylisobutylketone and carbon tetrachloride.

(ii) Distilled water, conforming to the specification given in the ASTM standard (Roberta, 1988) was used throughout this work.

(b) Sampling and Preservation

Samples of the effluent for the above study were collected on three different days from the final discharge of the oil refinery, in 2.5 litres capacity, clean amber coloured bottles. 6 ml of concentrated HCl was added for adjusting the pH of the effluent to below 2. At this pH, metals remain in soluble form.

(c) Sample Analysis

Every time ten portions of effluent, 400 ml each, from the effluent samples were transferred into ten 500 ml capacity volumetric flasks identified as A1, A2, A3, A4, A5, A6, A7, A8, A9 and A10. Samples A1, A6 were analysed immediately for the estimation of heavy metals.

It was found that the samples contain Fe, Cu, Ni, Zn, Pb and Cr in the concentration, given in Tables (1–3). Samples A2, A7 were analysed for the estimation of the above mentioned metals, after a sedimentation period of 24 hours. 200 mg calcium oxide was added to samples A3 and A8, 200 mg concentrated sulphuric acid was added to samples A4 and A9, and 200 mg hydrated aluminium sulphate was added to samples A5 and A10. After proper mixing, the samples were stored for 24 hours, to allow the settlement of any coagulated material. After expiry of the sedimentation period the supernatant liquid portions were analysed for the estimation of heavy metals. The same procedures were followed to analyse samples collected on other days, to evaluate the aggregation effect of the precipitating agents on the identified metal ions. The following Standard Procedures were used, for digestion, chelation, solvent extraction and estimation of content.

(*i*) *Digestion*

20 ml of HNO_3 and $HClO_4$ mixture in the ratio of (3:1) was added to each 200 ml of the supernatant fluid of the above prepared samples. All the samples were heated to boiling point and kept at the same temperature until the volume was reduced to 20 ml. After cooling, the mixture was diluted by the addition of 50 ml of distilled water. The pH of the samples Al to A5 was adjusted to 6 by adding diluted HCl and HNO_3, to estimate Fe, Cu, Ni, Zn and Pb. The pH of samples A6 to A10 was adjusted to 2, to estimate Cr.

(*ii*) *Chelation and solvent extraction*

For the treated samples (A1 to A5), 10 ml of 1% solution of 8-hydroxyquinoline was added with constant shaking. The chelated samples were transferred to a separatory funnel and extracted with three portions of 10 ml methylisobutylketone. The combined organic extracts were evaporated to dryness and the residue was dissolved in 20 ml of distilled water. The resulting solution was filtered to remove any undissolved precipitate. Similarly in each digested sample (A6 to A10), 10 ml of 1% solution of diphenylthiocarbazone was added with constant stirring, and the resultant chelated samples were extracted with three portions of 10 ml carbon tetrachloride. The combined organic extracts were treated similarly.

(d) Identification and Estimation of Contained Metals

The above prepared solutions were analysed by Atomic Absorbtion Spectrophotometer. The change in the concentration of the contained metals, either by sedimentation alone or with the addition of the above mentioned precipitating agents and simultaneous sedimentation, for the period of 24 hours, were computed and summarized in Tables 1–3 and elaborated in Fig. 1.

RESULTS AND DISCUSSION

As discussed above, calcium oxide, sulphuric acid and hydrated aluminium sulphate were used as precipitating agents. The metal ions are present in the aqueous solution (effluent) in soluble or suspended form. The precipitating agents adsorb these microfine metal particles on their surface and settle under gravitational force. It was found that by addition of calcium oxide in the concentration of 500 ppm, in the refinery effluent and simultaneous sedimentation of the same effluent, for the period of 24 hours reduced the percentage concentration of iron, chromium, copper, nickel, zinc and lead approximately to 96, 48, 82, 52, 92 and 94 wt.% repectively. Reduction by the sedimentation alone was only 62, 21, 57, 18, 49 and 53 wt.% respectively. So, the addition of calcium oxide further decreased the concentration by 34, 27, 25, 34, 43 and 41 wt.% respectively.

On the other hand the addition of hydrated

Table 1. Effect of Aluminium Sulphate Octadecahydrate, Calcium Oxide and Sulphuric Acid on Precipitation of Iron and Chromium Present in the Refinery Effluent. Concentration was Estimated after 24 Hours Sedimentation

Sample No.	Metal content in ppm					Reduction in metal concentration, in samples type A,B,C, and D, in wt%.			
	In fresh samples	In sedimented samples containing no chemical coagulant (Samples A)	In sedimented samples containing 500 ppm CaO (Samples B)	In sedimented samples containing 500 ppm H_2SO_4 (Samples C)	In sedimented samples containing 500 ppm $Al_2(SO_4)_3.18H_2O$ (Samples D)	(A)	(B)	(C)	(D)
Fe 1	0.35	0.14	0.01	0.13	0.02	60.00	97.14	62.86	94.29
2	0.52	0.20	0.02	0.19	0.03	61.54	96.15	63.46	94.23
3	0.35	0.13	0.01	0.13	0.02	62.86	97.14	62.86	94.29
4	0.51	0.19	0.02	0.19	0.03	62.75	96.08	62.75	94.12
5	0.53	0.20	0.02	0.20	0.03	62.26	96.23	62.26	94.34
6	0.45	0.17	0.02	0.17	0.02	62.22	95.56	62.22	95.56
Average:	(0.45)	(0.17)	(0.02)	(0.17)	(0.03)	(61.94)	(96.38)	(62.74)	(94.47)
Stand. dev.	(+0.19)	(+0.03)	(+0.01)	(+0.03)	(+0.01)	(+1.06)	(+0.63)	(+0.46)	(+0.54)
Cr 1	0.34	0.27	0.18	0.24	0.13	20.59	47.06	29.41	61.76
2	0.36	0.29	0.19	0.26	0.13	19.44	47.22	27.78	63.89
3	0.34	0.27	0.18	0.24	0.13	20.59	47.06	29.41	61.76
4	0.36	0.29	0.19	0.26	0.13	19.44	47.22	27.78	63.89
5	0.35	0.27	0.18	0.25	0.13	22.86	48.57	28.57	62.86
6	0.36	0.27	0.18	0.24	0.13	25.00	50.00	33.33	63.89
Average:	(0.35)	(0.28)	(0.18)	(0.25)	(0.13)	(21.32)	(47.86)	(29.38)	(63.01)
Stand. dev.	(+0.01)	(+0.01)	(+0.01)	(+0.01)	(+0.00)	(+2.19)	(+1.20)	(+2.07)	(+1.05)

Table 2. Effect of Aluminium Sulphate Octadecahydrate, Calcium Oxide and Sulphuric Acid on Precipitation of Copper and Nickel Present in the Refinery Effluent. Concentration was Estimated after 24 Hours Sedimentation

Sample No.	Metal content in ppm					Reduction in metal concentration, in samples type A,B,C, and D, in wt%.			
	In fresh samples	In sedimented samples containing no chemical coagulant (Samples A)	In sedimented samples containing 500 ppm CaO (Samples B)	In sedimented samples containing 500 ppm H_2SO_4 (Samples C)	In sedimented samples containing 500 ppm $Al_2(SO_4)_3.18H_2O$ (Samples D)	(A)	(B)	(C)	(D)
Cu 1	0.38	0.16	0.07	0.15	0.04	57.89	81.58	60.53	89.47
2	0.11	0.05	0.02	0.04	0.01	54.55	81.82	63.64	90.91
3	0.38	0.16	0.06	0.15	0.04	57.89	84.21	60.53	89.47
4	0.44	0.19	0.08	0.18	0.05	56.82	81.82	59.09	88.64
5	0.45	0.19	0.08	0.18	0.05	57.78	82.22	60.00	88.89
6	0.46	0.20	0.08	0.18	0.05	56.52	82.61	60.87	89.13
Average:	(0.37)	(0.16)	(0.07)	(0.15)	(0.04)	(56.91)	(82.38)	(60.76)	(89.42)
Stand. dev.	(+0.30)	(+0.06)	(+0.02)	(+0.06)	(+0.03)	(+1.30)	(+1.05)	(+1.53)	(+0.80)
Ni 1	0.46	0.37	0.22	0.46	0.37	19.57	52.17	Nil	19.57
2	0.56	0.46	0.27	0.56	0.45	17.86	51.79	Nil	19.64
3	0.32	0.26	0.15	0.32	0.26	18.75	53.13	Nil	18.75
4	0.29	0.24	0.14	0.29	0.24	17.24	51.72	Nil	17.24
5	0.28	0.23	0.13	0.28	0.23	17.86	53.57	Nil	17.86
6	0.31	0.25	0.15	0.31	0.25	19.35	51.61	Nil	19.35
Average:	(0.37)	(0.30)	(0.18)	(0.37)	(0.30)	(18.44)	(52.33)	(–)	(18.74)
Stand. dev.	(+0.11)	(+0.09)	(+0.06)	(+0.11)	(+0.09)	(+0.93)	(+0.82)	(–)	(+0.99)

Table 3. Effect of Aluminium Sulphate Octadecahydrate, Calcium Oxide and Sulphuric Acid on Precipitation of Zinc and Lead Present in the Refinery Effluent. Concentration was Estimated after 24 Hours Sedimentation

Sample No.	Metal content in ppm					Reduction in metal concentration, in samples type A,B,C, and D, in wt%.			
	In fresh samples	In sedimented samples containing no chemical coagulant (Samples A)	In sedimented samples containing 500 ppm CaO (Samples B)	In sedimented samples containing 500 ppm H_2SO_4 (Samples C)	In sedimented samples containing 500 ppm $Al_2(SO_4)_3.18H_2O$ (Samples D)	(A)	(B)	(C)	(D)
Zn 1	0.62	0.32	0.05	0.47	0.17	48.39	91.94	24.19	72.58
2	0.62	0.32	0.05	0.47	0.18	49.11	91.94	23.81	71.45
3	0.66	0.34	0.06	0.50	0.18	48.48	90.91	24.24	72.73
4	0.68	0.35	0.06	0.52	0.18	48.53	91.18	23.53	73.53
5	0.64	0.33	0.05	0.49	0.17	48.44	92.19	23.44	73.44
6	0.64	0.33	0.05	0.49	0.17	48.44	92.19	23.44	73.44
Average:	(0.64)	(0.33)	(0.05)	(0.49)	(0.18)	(48.57)	(91.73)	(23.76)	(72.86)
Stand. dev.	(+0.18)	(+0.01)	(+0.01)	(+0.02)	(+0.01)	(+1.27)	(+0.55)	(+0.24)	(+0.08)
1	0.88	0.41	0.05	0.57	0.04	53.41	94.32	35.23	95.45
2	0.92	0.43	0.05	0.60	0.04	53.26	94.57	34.78	95.65
3	0.68	0.32	0.04	0.44	0.03	52.94	94.12	35.29	95.59
4	0.68	0.32	0.04	0.44	0.03	52.94	94.12	35.29	95.59
5	0.68	0.31	0.04	0.44	0.03	54.41	94.12	35.29	95.59
6	0.66	0.31	0.04	0.43	0.03	53.03	93.94	34.85	95.45
Average:	(0.75)	(0.35)	(0.40)	(0.49)	(0.03)	(53.33)	(94.20)	(35.12)	(95.55)
Stand. dev.	(+0.12)	(+0.05)	(+0.01)	(+0.08)	(+0.01)	(+0.56)	(+0.22)	(+0.20)	(+0.08)

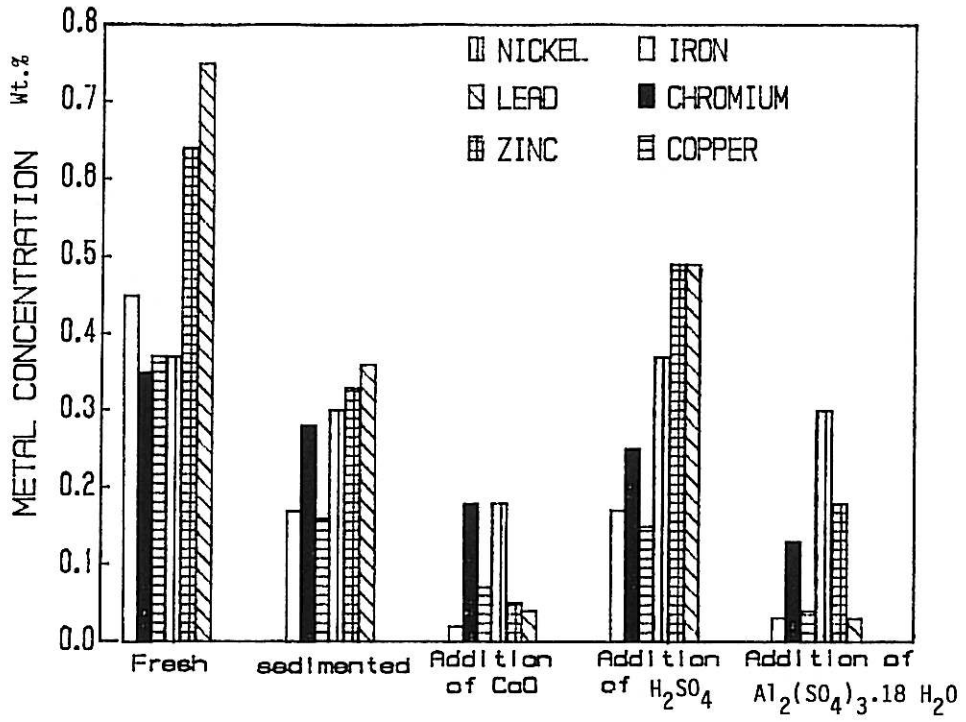


FIG. 1. Reduction of metal concentrations by sedimentation and the addition of coagulants.

aluminium sulphate in the concentration of 500 ppm, in the effluent and simultaneous sedimentation for a period of 24 hours reduced the percentage concentration of these metal ions approximately to 94, 63, 89, 19, 73 and 96 wt.% respectively. The increase in the percentage reduction was calculated to be 32, 42, 32, 1, 24 and 43 wt.% respectively.

The addition of sulphuric acid in the effluent, in a concentration of 500 ppm and simultaneous sedimentation for 24 hours, reduced the percentage concentration of the metals approximately to 63, 29, 61, zero, 24 and 35 wt.% respectively. Further reduction in the percentage concentration of iron, chromium and copper was observed while an oppo-

site effect was found in case of nickel, zinc and lead metals.

Regarding the degradation mechanism, calcium oxide and aluminium sulphate octadecahydrate, upon disolution in aqueous medium, are converted into insoluble hydroxides. These hydroxides act as metal scavangers and adsorb the microfine metal ions from the medium. The following model equations explain the aggregation of metal ions as metal hydroxide. Metal hydroxide in the aqueous medium converts into positive or negative charged particles depending on the pH of the medium, as shown below:

$$M(OH)_n + H^+ \rightarrow [M(OH)_{n-1}(OH_2)]^+$$

$$M(OH)_n - H^+ \rightarrow [M(OH)_{n-1}(O)]^-$$

The postive charged particles of the metal hydroxide assist in aggregating the negative charged metal ion complexes. The negative charged metal hydroxide ion attracts the positive charged metal ions and bring out their sedimentation. Metal ions which carried ligands form bonds with metal hydroxide by displacement of either hydrogen ion or hydroxil ion, depending on the pH of the medium. The possible metal ligand bonding may be as follows:

$$\begin{matrix} M-OH \\ \\ M-OH \end{matrix} \quad + Mt^{z+} \longrightarrow \quad \begin{matrix} M-O \\ \diagdown \\ Mt^{z-2} + 2H^+ \\ \diagup \\ M-O \end{matrix}$$

Mt^{z+} = Metal pollutants

or

$$M(OH)_n + Mt^{z+}L \overset{-H^+}{\rightleftharpoons} M(OH)_{n-1} \cdot OMt^{z-1}L$$

$$M(OH)_n + Mt^{z+}L \overset{+H^+}{\rightleftharpoons} M(OH)_n \cdot HMt^{z+1}L$$

But there is a reversible equilibrium between the metal ions or metal complexes already sorbed by the metal hydroxide and the metal ions or complexes present in the aqueous medium. The change in concentration of any of the species brings change in the concentration of other species in the reaction vessel, as shown below:

$$\begin{matrix} Mt^{z+}\ (\text{sorbed}) & \rightleftharpoons & Mt^{z+}\ (\text{aqueous}) \\ \uparrow\downarrow & & \uparrow\downarrow \\ Mt^{z+}L\ (\text{sorbed}) & \rightleftharpoons & Mt^{z+}L\ (\text{aqueous}) \\ \uparrow\downarrow & & \uparrow\downarrow \\ L\ (\text{sorbed}) & \rightleftharpoons & L\ (\text{aqueous}) \end{matrix}$$

Sulphuric acid acts as precipitating agent only if the medium is able to convert sulphate ions into sulphide ions. These sulphide ions are metal precipitants, which convert metal ions into insoluble metal sulphides. Desulfovibrio bacteria are responsible microorganisms for the conversion of sulphates ions into sulphides ions. From the experimental results, it has been found that the effluent does not contain these bacterias and sulphate ions remain in the medium as such. Due to the high concentration of sulphate ions, metal ions are converted into soluble metal sulphates.

CONCLUSION

It has been proved that calcium oxide and hydrated aluminium sulphate are suitable precipitants for metal ions present in the refinery effluent and can be added in concentration of 500 ppm in the refinery effluent, for reducing the concentration of heavy metal ions, when they exceed the thresh-hold limits. These chemical substances are cheaper and available. They have appreciable efficiency when used in the concentration mentioned.

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