



High molecular-weight polymer flocculation treatment of waste water and sludge from mineral processing plants

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ABSTRACT

Even though the choice method of waste water and sludge impoundment in settling ponds by mineral processing and metallurgical plants, chemical manufacturing, pharmaceutical and textile mills in Nigeria has not fully helped in the recovery of valuable minerals and metals, nor the water associated with it. Yet is very unfortunate that only few plant in Nigeria use the impounding and settling ponds; and where these are constructed, they occupy very large area of land which are afterward difficult to be reclaimed and pose environmental hazard such as breeding of ecologies like bacteria, mosquitoes (carrier of malaria parasites) and host of others. In the industrial cities like Lagos and Port Harcourt, industrial effluents are often seen, running into the street waterways, while very small quantities are channelled for treatment by the companies concerned. The result of a work done on the treatment of stream water and sludge (effluents) collected from a sand mining deposit and some mineral processing plants using high molecular polymers (HMP) as flocculants is being reported in this paper. The water samples were treated with common conventional dewatering methods such as the use of lime and bentonite. High molecular polymers such as Nalco 7191[®] and PEO[®] were also used to dewater these waste effluents. With the use of 0.02g/l PEO, 0.07g/l Nalco 7191[®] and 0.05g/l Percol 351[®], the water clarity and % dewatering were brought to 88, 16, 280 NTU and 55%, 43% respectively after 24hrs. The dewatered solid could be handled mechanically, was not thioxotropic and hence suitable for landfill.

Key words: Treatment, wastewater, sludge, processing plant, high molecular polymers, flocculants, dewatering, minerals processing, thioxotropic, metal extraction, ultra-fine particles.

INTRODUCTION

Nigeria is blessed with many natural resources such as water, minerals, petroleum, green vegetations and climates and so on. Many mineral deposits have been discovered for long time in past, some of which processing have reached the advanced stages [1]. Iron ore mining and beneficiation plants are located at Itakpe and are take over by private managers; cement industries are found in some other parts across the country (Figure 1) such as Ewekoro, Sagamu, Obajana, Sokoto and Bauchi, glass plants are located at Igbokoda in and Ikorodu, both in south-western political zone of Nigeria to mention a few while baryte is mined and processed at Azara; coal at Enugu, tin and kaolin processing at Jos, limestone and marble cutting and polishing at Jakura and Lokoja, and vast of many other metallurgical, mineral processing and extraction plants [2, 3].

Many operations in mineral processing and metal extraction make use of water in very large quantities. Mineral industries source for water and locate very close to it. In the processing of minerals and some other industrial products, wastewaters containing some appreciable quantity of heavy metals and ultra-fine particles, which have very poor response to the known conventional physical separation techniques used in water treatment, are discharged into the water bodies (surface and underground).



Figure 1: Map showing some industrial cities in Nigeria (MS Encarta Premium 2009)

These metals and minerals bearing effluents often result in losses of metal values and on the other hand, when discharge into water bodies result to environmental pollution. In Nigeria, the discharge of the numerous effluent poses serious threats to the neighbouring communities. The shortfall in supply of treated portable water often results in searching and depending on various sources of unclean water. On the other hand, where there are pipe borne water, people crowd around the taps and extraordinary long queue are often experienced (Figure 2). These result in frustrations and hostility of the hosting communities to these industries especially, the oil companies. Though the method of impoundment in settling ponds has not fully helped in the recovery of valuable minerals and metals, nor the water associated with it. It is also unfortunate that only few industries in Nigeria use the impounding and settling ponds, and where these are constructed, they occupy very large area of land which are afterward difficult to be reclaimed and pose environmental hazard such as breeding of ecologies like bacteria, mosquitoes (carrier of malaria parasites) and host of others. In the industrial state like Lagos, Industrial effluents are often seen, running into the street waterways, while very small quantities are channelled for treatment.



According to the study of World Health Organisation (WHO) in 1980, at least 30,000 people die every day in developing countries of the World because of unsafe water supplies [4].

Water pollution is increasing and becoming severe day-by-day and posing a great risk to human health and other living organisms also reported to be an acute problem almost in all major rivers and dams in India by Mane et al, 2013[5]. US government, the UN and some other International organisations such WHO, UNISEF, DIFRI, etc had invested multi million dollars in various millennium goal projects involving the provision of portable water and the eradication of malaria parasites from the west Africa sub-region including Nigeria. The vitality and scarcity of good naturally existing water resources and the need to recover many valuable metals lost into the industrial effluents, and

the need to meet the standard regulations of WHO on water have continuously led to many research works on the determination of the quality and quantity and removal of unwanted hazardous elements (metals and minerals) naturally found or resulting from processing industries and thus also concerned about investigation on various methods of water treatment and dewatering method. Among such works were reported by Pahlman and Khalafalla 1988 [6], Holland 1988 [7]; Reis and Cordeiro 2013 [8]; Jong et al 1989 [9]; Hood and Smelley, 1991 [10]; Nilsen et al, 1991 [11]; and Jeffers et al, 1991 [12].

Sani et al, 2012 [13] used AAS to determine the concentration of Aluminium, Iron, Zinc, Lead, Cobalt, Nickel and Chloride in the various water samples from different locations within University of Maiduguri, community. From the results, the majority of the show concentrations that are above the WHO recommendation. In one of south-western area, Adewole et al, (2011) [14] studied the physico- chemical properties of 50 years and 150 years old cocoa farms soils were analyzed for their pH, total nitrogen, phosphorus, particle sizes and mineral analyzes. The mineral analyses showed that the mineral contents ranged from 0.045 ± 0.05 mg/kg to 0.52 ± 0.03 mg/kg while the soil samples showed traces of heavy metals like Pb, Mn, Ni, Cd. In another instance, Yu et al, 2014 [15] of recent reported studies on the effect of different salinity water irrigation and soil salt contents on maize growth. The results showed that the salinity water had much greater effect on maize emergence rate than that of soil initial salt content.

The effect of the pre-selection of particle size range on the treatment of locally-sourced bentonite clay from Logomani, North-Eastern Nigeria using aqueous acid and alkali solution has been studied by Nwokem et al, 2014 [16]. In the report, the characterization of the clay adsorbents was done via Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction analyses (XRD). The acid (2.5M of HCl and H₂SO₄) and alkali (0.5M NaOH) modified clay adsorbents were applied in the removal of methylene blue from aqueous media. The performance efficiency of acid treated asphaltic carbon (H₂SO₄-AC) and base treated asphaltic carbon (NaOH-AC) with respect to adsorption of Cu²⁺, Cr⁶⁺ and Pb²⁺ from waste water was studied by Ambursa et al, 2011 [17]. The activated carbon was produced from asphalt by treatment with H₂SO₄ and NaOH as activating agents. The result show that the efficiency of acid treated asphaltic carbon (H₂SO₄-AC) is high than Base treated asphaltic carbon (NaOH-AC) for removal of Cu²⁺, Cr⁶⁺ and Pb²⁺ ions from wastewater.

The present study considers the treatment of polluted natural stream water and waste sludge (effluents) from some selected Nigerian based mineral processing plants [20, 21] using high molecular polymers as flocculants being guided by the various recommended practices by the US Bureau of Mine [6,7, 9, 10, 11, 12]

EXPERIMENTAL SECTION

Materials: Waste effluents (sludge and waste water samples) were obtained from some mineral processing plants located in Nigeria including: West Africa Portland Cement Plc Ewekoro plant; Azara baryte processing plant of the Nigeria Mining Corporation; Glass and Ceramic pilot plant of the Federal Polytechnic, Ado-Ekiti; Mineral processing and Beneficiation workshops of National Metallurgical Development Centre, Jos; National Iron ore Mining Company, Itakpe and water samples was gotten from sand mining deposits within Ado Ekiti and Akure metropolises. The five selected samples were designated as A, B, C, D and E respectively. Treatment chemicals such as Mg(OH)₂, lime, alum, bentonite and CaCl₂ were procured while PEO[®], Nalco 7191[®] and Percol 351[®] were obtained from OSRC Water Scheme, Osogbo. The cationic polymer (Nalco 7191) and the non-ionic polymer (Percol 351) were used in place of Nalco 7110[®] and Percol 333[®] previously reported by Hood and Smelley, 1991 [10].

Experimental Procedure

5ml of water samples were taken from each source for chemical analysis by atomic absorption spectrometric AAS method and the result is presented in Table 1.

100ml of sludge or water samples were measured in each case for small scale treatment. The weighed sample was pre-treated by the addition of specified quantities of additives and catalysed by mechanical agitation in a beaker using an impeller. The drops of aqueous solution of the flocculants were added using graduated burette.

The mixture was transferred to a magnetic stirring bar for thorough stirring and to get a consolidation points for flocculation (the point at which the flocs move in the beaker as a unit solid mass). The supernatant water is screened until flocs could be handled, squeezed or filter-pressed and the volume of water loss was measured and the solid content of the flocculated solid was determined. The consumptions of the flocculants were determined from the burette reading and the dosage is calculated in gram per litre (g/l) of the effluent.

The mixtures of the samples collected were treated with various dosages of chemical additives such as lime, CaCl₂, bentonite and with high molecular-weight polymers-HMP (Nalco 7191[®], Percol 351[®] and PEO[®]). The parameters

that were determined include the water clarity, Nephelometric Turbidity Unit (NTU), chemical dosage (g/l) and the dewatered solid waste (%).

pH measurement

The pH of the samples was measured using electronic digital mV-Temperature-pH meter (model PHS-3BW). The electrodes of electronic thermopile and digital pH-mV-temperature meter were immersed in the vessel containing the water samples and the pH was directly measured with the electrode, while pH of the sediment sample was measured by preparing (1:5, sediment: water) suspension in distilled water. The contents were stirred well and allowed to settle and supernatant was used to check pH according to Mane et al, 2013 [5] and Egunlae [18].

Total Dissolved Solid (TDS)

The Total Dissolved Solids (TDS) of a solution is the concentration of dissolved solids in it. TDS of the water samples and sediment suspension was measured by using TDS meter (PHS-3BW) where electrode was inserted directly into the sample solutions for the direct display of results on a digital scale as a reading in mg/l.

Total Hardness of Water sample

The total hardness of the water samples was determined by standard EDTA titration method with 1-2 ml buffer of pH = 10 and a droplet of Eriochrome black-T indicator.

$$\text{Hardness (mg/l)} = V \times T \times 1000 / \text{ml of Sample}$$

Where V = Titre volume (ml) of EDTA, T = mass (mg) of CaCO₃ equivalent to 1.0 ml of EDTA

Heavy Metal Analysis in water and sludge samples using AAS:

Heavy metals were detected by using atomic absorption spectrometer AAS (Thermo-series 2000) [19].

RESULTS AND DISCUSSION

Results of chemical analyses of as-collected sludge and water samples are presented in Tables 1 and 2 respectively. The waste effluents and sludge sample (A, B and C) were obtained from ceramic-based industries hence solids in the samples consist mostly of clay, feldspar, frit silica and baryte. The sludge sample initially containing about 67% solid was diluted 25% solid prior to testing. This tend to stimulate the sludge and to allow the flocculant to structure the floc into a stronger tougher sludge. The pre-treatment of sludge with various dosages of bentonite, lime and CaCl₂, readily flocculate with high molecular weight polymers and hence there was improvement in flocculation of the fine solids.

Table 1: Chemical analyses of sludge and waste water samples

Constituents (mg/l)	Sample A	Sample B	Sample C	Sample D
BaSO ₄	-	60.40	-	-
Fe ₂ O ₃	2.29	4.23	0.94	1.98
SiO ₂	13.37	17.7	21.61	32.68
Al ₂ O ₃	3.79	3.83	4.13	2.31
TiO ₂	N.A.	0.004	0.012	0.06.
MgO	1.79	0.35	0.84	0.73
Na ₂ O	0.68	N.A	0.92	-
CaO	41.41	0.12	40.2	3.8
SiO ₂	N.A	0.001	N.A	N.A
K ₂ O	0.31	N.A	0.64	N.A
Pb ⁺	-	-	-	1.01
Zn ⁺	-	-	-	0.42
Trace metals	0.23	0.19	0.12	0.27
Total CO ₃	77.67	-	-	-

N.A = Not Available.

Table 2: Analysis of natural stream water sample from sand mining site (Ado, WHO)

Sample	SO ₄	pH	K	Na	Ca	Mg	Cu	Fe	Cl	TDS	Alkalinity	TUR	Colour
WHO standard	500	6.5-9.2	20	200	200	150	0.1	0.1	250	1000	500	50	50
Ado	49	6.9	22	10.2	15.24	25.79		0.09	0.05	200	90.1	10	40

Table 3 shows the result of flocculation using lime, bentonite and CaCl₂. The result shows a similarity in the behaviours of lime and CaCl₂ having equal dosage consumption. With the application of , (9.5 g/l) bentonite, 0.15 g/l PEO was used up bringing the clarity of water from 1320 NTU to 560 NTU after 24hrs at 44% dewatering of

solid. The best result was obtained from the use of 0.05 g/L PEO without other additives. The water clarity improved to 982 NTU at 52% solids.

Table 3: Result of lime tests on sludge mixture

Specimen designation	Additives	Additive dosage (g/l)	PEO (g/l)	Separation (Immediate)	Separation (After 24 hrs)	Dewatered solid (%)
a	Lime	2.40	0.4	NS	NS	NS
b	Bentonite	9.50	0.15	1,320	560	44
c	CaCl ₂	2.40	0.2	NS	NS	N.S
d	No-additive	-	0.05	1,380	982	52

N.S. = No Separation.

In Table 4, the improvement of water clarity was perfected by the PEO treatment of the four (4) effluent samples. They were pre-treated with CaCl₂ and bentonite before dewatering with PEO. The rest results obtained in Table 5 show that the high molecular polymer flocculation process was effective over the sampling range, as sludge containing 48 to 61% solids and 6-8 NTU clarity was produced from the four water/sludge samples. This result compares favourably with a close range of conclusion the similar field test by Hood and Smilley, 1991 [10] which produced a result of 47-58% solids and water clarity of 4-20 NTU from set of seven water and sludge samples used. From the present study, the results show that these additives can be used in treating waste effluents from minerals and metallurgical industries. The dewatered solid could be handled mechanically was not thixotropic and hence suitable for landfill purpose.

Table 4: Result of polymer flocculation test on sludge mixture

Polymer additive	Polymer dosage (g/l)	Separation Immediate	Separation After 24hrs	Dewatered solid (%)
PEO [®]	0.02	2.20	88	55
Nalco 7191 [®]	0.07	400	16	43
Percol 351 [®]	0.05	640	280	74

Table 4 compares the result of polymer flocculation test on the four-sludge mixture using PEO[®], Nalco[®] and Percol[®]. The result shows that PEO[®] has the best flocculation result on this mixture based on the dosage effectiveness. At 0.02g/l PEO[®] consumption clarity of 220 NTU and 88 NTU were obtained at 55% dewatering solid immediately and after 24 hrs of treatment respectively. Nalco 7191 shows highest dosage consumption of 0.07g/l and at the least % dewatering of 43%. The use of Percol 351[®] in sludge treatment will actually produce dewatered solid of high quality suitable for land fill purpose [20, 21]

In Table 5, the result of the effect of optimum dosage of the additives (bentonite and CaCl₂) and PEO[®] in the treatment of the four sludge samples and a water sample were examined and compared.

Table 5: Determining the effect of optimum dosages of additives on sludge samples

Sample	Initial solids (%)	Additive bentonite (g/l)	Dosage CaCl ₂ (g/l)	PEO [®] g/l	NTU Immediate	NTU After 24hrs	Dewatered solid (%)
A	2.1	1.2	1.2	0.02	125	7	53
B	3.1	1.2	1.2	0.04	480	6	61
C	0.7	1.2	1.18	0.03	98	8	48
D	0.8	1.2	1.16	0.02	32	8	50
E	0.3	1.2	1.2	0.02	15	2	7

CONCLUSION

In the present investigation, an attempt has been made to assess water treatment and metal recovery of heavy metals present in the sediment of the selected waste water. The four samples collected from different locations showed higher levels of heavy metals and is the clear indication of contamination. Base on the data obtained from the laboratory dewatering tests conducted on lime treated sludge from these mineral plants, three polymers were tested as flocculants to determine their ability to dewater the effluents. Among all, PEO[®] was found to be most effective and also other additives such as clay, bentonite and CaCl₂ were effectively utilized in pre-treating the waste sludge prior to dewatering by PEO[®] thus improving the water clarity. Based on the laboratory results obtained, a designed research is currently proposed for a continuous onsite dewatering test using these dewatering techniques to be conducted in these plants. Further research studies are needed and encouraged with an extensive scope and continuous study on the characterisation of the sludge for other major industrial effluents and pollutants and

monitoring the extent of the environmental influence [18, 19, 20, 21]. More representative samples should be used to go beyond this initial assessment as reported in this study.

REFERENCES

- [1] OO Onyemaobi, Proceedings of NSE 2001 National Conf/AGM. Port Harcourt, **2001**, Nov 5-9,
- [2] MAU Nwoke, *Nigerian Mining Journal*, **1997**, 2 (1) 42-55
- [3] OO Egunlae; Oloruntoba DT, *Proceedings of 2002 Nigeria Materials Congress and AGM, Nov 11-13, 2002*. 1(1): 200-202.
- [4] H EI-Fadaly; MM EI-Defrawy; F EI-Zawawy; D Makia, Pakistan J of biological Sciences, **2000**, 3 (5), 777- 781, In Tambekar P.; Batra R.J; Weginwar R.G. India. *J. Chem. Pharm. Res*, **2014**, 6(5):710-714
- [5] AV Mane; RG Pardeshi; VR Gore; Walave RL; Manjrekar SS; Sutar GN; *J. Chem. Pharm. Res*, **2013**, 5(8), 91-102
- [6] JE Pahlman; Khalafalla S. E. *US Bureau of Mines Rep. Inv.* **1988**, RI9200
- [7] PW Holland, *US Bureau of Mines PA*, **1988**, PA28933
- [8] RF Reis; Cordeiro J. S. In 11th Global conf on sustainable Man., 23-25 September **2013**, Berlin, Germany, *GCSM-IRP*. **2013**, 121-124
- [9] BW Jong; Rhoads SC; Stubbs AM; Stoelting TR. *US Bureau Mines Rep. Inv.* **1989**, RI 9252
- [10] GD Hood; Smilley AG. *US Bureau Mines Report of Investigation*, **1991**, RI9376.
- [11] DN Nilsen; BW Jong; Stubbs AM, *US Bureau Mines Report of Investigation*, **1991**, RI9375.
- [12] TH Jeffere; Ferguson CR; Bennelt PG. *US Bu. Mines Report of Inv*, **1991**, -RI9340
- [13] A Sani; A Jibir; ET Alemikab; MA Sani; RO Abdulraheem; SS Abdulkareem; RB Abdulraheem; M. Ilyas. *J. Chem. Pharm. Res*, **2012**, 4(8):3855-3860
- [14] E Adewole; Ogunmodede OT; Talabi J; Ajayi OO; Oso OA; Lajide L. *J. Chem. Pharm. Res.*, **2011**, 3(6):544-552
- [15] X Yu; Liao Y; Oladipo IO; *J. Chem. Pharm. Res*, **2014**, 6(1):300-305
- [16] CO Nwokem; Gimba CE; Ndukwe GI; Abechi SE. *J. Chem. Pharm. Res.*, **2014**, 6(4):637-647.
- [17] MM Ambursa; UZ Faruk; A Uba; DM Sahabi; FA Atiku; RA Koko. *J. Chem. Pharm. Res.*, **2011**, 3(6):732-741
- [18] OO Ajibola; BO Jimoh. *Advances in Applied Science Research*, **2014**, 5(3) :68-72
- [19] OO Ajibola; BO Adewuyi; DT Oloruntoba, *International Journal of Innovation and Applied Studies*, **2014**, 6(3): 420-430
- [20] OO Egunlae, *International Research Journal in Engineering, Science and Technology*, **2011**, 8(1) 1-9.
- [21] OO Egunlae, *International Research Journal in Engineering, Science and Technology*, **2011**, 8(1) 33-42.