Journal of Himalayan Earth Sciences Volume 53, No. 2, 2020 pp. 60-69

UP-Gradation of black shale of Chimiari region of Pakistan by flotation scheme

Muhammad Tahir[1], Zahid Ur Rehman[2*], Sajjad Husain[2], Noor Muhammad[2], Muhammad Nazir[1], Muhammad Sadiq[1], and Iltaf Hussain[3]

[1]*Pakistan Atomic Energy Commission, Islamabad*

[2]*Department of Mining Engineering, University of Engineering & Technology, Peshawar*

[3]*Department of Basic Sciences and Islamiat, University of Engineering & Technology, Peshawar*

**Corresponding author's email: engr.zahid@uetpeshawar.edu.pk*

Submitted date:21/07/2020 Accepted date:12/11/2020 Published online:

Abstract

With the increasing demand and depletion of high-grade ore deposit, attention is being diverted to recover the need from previously ignored, low grade ore deposits. Th low grade ores are being processed by the different advance techniques of mineral processing. In this research Black Shale of Chimiari region of Khyber Pakhtunkhwa, Pakistan was processed by floatation technique with three different reagents i.e. collectors (Sodium Amyl Xanthate and Sodium Ethyl Xanthate, triton-x-100), frothers (methyl isobutyl carbinol (MIBC) and Pine oil) and depressant (sodium silicate) with varying dosage rates as well as particle size. Three different anionic collectors, one from oxyhydryl group (triton-x-100) and others from sulphydryl group (xanthates) have been tested. Results shows that Triton-X-100 gives highest recoveries among three collectors however, grades were not improved. Sodium ethyl xanthate gives more improved results for Cu, Zn, Ti and V etc. than sodium amyl xanthate. Keeping in view the grade –recovery aspect of Total carbon content (TCC), it was observed that a dosage rate of 200 g/t of sodium amyl xanthate give better results than triton-x-100 and sodium ethyl xanthate. Two frothers from neutral category, Methyl iso-butyl carbinol (MIBC) and Pine oil were also tested and it was found that the performance MIBC was impressive than Pine oil at same dosage rates. Sodium Silicate was used as depressant for the gangue minerals (clay and silica) and results reveals that at dosage rate of 1.5 kg/t , clay minerals were depressed more than silicate. Similarly, tests were performed with heads of four particle sizes ranges of -53, -106+53, -150+106 and -212+150 microns respectively. Particle size analysis reveals that fine grinding improves recovery of TCC from 45% to 68%, while grads decreased. It was also found that fine grinding also improves recovery of heavy metals. The analysis of floated fractions with XRF and ICP-OES, also confirm the up-gradation of many base and heavy earth metals.

Keywords: Black shale, Flotation, Recovery, Up-Gradation

1. Introduction

Mineral and ore deposits subject to their metallic content and distribution have been categorized as high and low grade (Wills, 2006). It is easy to extract mineral of interest from higher grade ores; however, the availability of high-grade ores is rapidly decreasing with the depletion of high-grade deposits and increasing demand of metal. Attention is being diverted to recover the need from previously ignored, low grade ore deposits. The characterization of Black shale shows that it is one of the potential resources of multi-metal low grade ores and it has been reported that most of the heavy earth metals occur in the matrix of carbonaceous content (Vernon, 1961; IAEA, 2009).

Various Mineral beneficiation and up-gradation techniques and its further processing to extract metals have been mannered for extracting metals from these low-grade sources (Wills, 2006). These methodologies, based on their working principles are recognized as physical, chemical, physio-chemical, or microbiological separation techniques. Many chemical and microbiological upgradation have been tested for black shale upgradation however, none of these is found economically feasible because of the huge quantity of gangue material techniques (Smith et al., 1993; Das et al., 1999; Santhiya et al., 2001; Sharma, 2001; Smith and Miettnen, 2006; Wills, 2006, 2006; Langwaldt & Kalapudas, 2007; Bhatti & Butt, 2007; Bhutti et al., 2013) . Other problems which pose significant limitations both on mining and processing of low-grade sources include a) disseminated nature of metallic content, b) complex mineralogical characterizations and c) extremely low metallic contents (grades). One of the reasonable ways to come out of such critical situation is to pre-concentrate the feed before final recovery (IAEA, 1993; Bhutti et al., 2013).

Physical techniques of up-gradation, such as flotation, gravity separation, magnetic separation, radiometric and optical sorting etc. are more often used for pre-concentration of ores (IAEA, 1993; Bhatti et al., 2007; Bhutti et al., 2013). In the present work, flotation scheme is studied as a pre-concentration methodology to upgrade the carbonaceous content of the black shale of Chimiari region of Pakistan. The study aims to test the response of flotation in terms of concentration of carbonaceous content at various types and dosage rates of flotation reagents and also presents the effect of particle size on grade and recovery.

2. Materials and methods

2.1 Sample characterization of Chimiari black shale

Sample of black shale is taken from Chimiari region of KPK, Pakistan. The area is located in the “Baghdarra Fault” region of Ghandghar range (Southern Hazra area in fold and thrust belt of Himalaya) near the village Chimiari (Ruskeeniemi, and Heino,1996; Bhutti et al., 2013). Sample 11kg was taken as broken pieces of core and crushed with Blake type jaw crusher and then pulverized with disc mill. This sample was then subjected to coning and quartering repeatedly and finally sieved to required sizes.

Each grounded sample was characterized for its elemental, chemical and mineralogical composition by wavelength- dispersive type XRF (X-ray florescence) and XRD respectively. Loss on ignition test was performed on selected samples to determine total carbon content (TCC) as shown in table 1.

Elemental composition of Chimiari black shale was found by WD-XRF using IQ+ software. It must be emphasized that these results are normalized to 100% and exact quantifications may vary. The results after normalization are presented in table 2.

Bhatti and Butt 2007; Bhatti et al., 2013 obtained the mineralogical characteristics which are presented in table 3.

Table 1. Total carbon content of Chimiari black shale.

Particle Size (micron)	Total carbon content (TCC)
Bulk (from total sample)	18.7 %
-212 (all particle sizes)	15.8 %
-53	17.4 %
-106+53	16.8 %
-150+106	14.4 %
-212+150	16.1%

Table 2. Elemental characteristics of Chimiari black shale.

Element	Concentration (%)
Cu	0.041
Ni	0.025
Zn	Nd
Cr	0.043
Ti	0.459
V	0.184
S	0.677

Table 3. Mineralogical characteristic of Chimiari black shale.

Mineral identified	Formula
Quartz	SiO_2
Graphite	C
K-Feldspar	$KAlSi_3O_8$
Biotite	$K(Mg,Fe)_3AlSi_3O10(OH)_2$
Chlorite	$(Mg,Fe_2+, Fe_3+)6AlSi_3O_{10}(OH)_8$
Phlogopite	$KMg_2(Si_3AlO_{10})OH_2$
Sericite	$K,Na,Ca,Mg,Fe,AlSiO_2OH$
Microcline	$KAlSi_3O_8$
Limonite	$Fe_2O_6.6H_2O$
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Kerogen	Hydrocarbon compounds

Chemical analysis of Chimiari black shale are carried out using ICP-OES (Inductive coupled plasma- optical emission spectroscopy) with partial dissolution in "aqua regia". The results are compiled in table 4.

2.2. Sample for floatation

Samples, each weighing 250g, were prepared at -212 microns for testing the response of flotation reagent dosage. To examine the effects of particle size, samples, each weighing 500g, in the particle sizes of -53, -106+53, -150+106 and -212+150 microns were used. With these samples three collectors (sodium ethyl xanthate, sodium amyl xanthate and triton-x-100), two frothers (MIBC and pine oil), one depressant (sodium silicate) were tested at different dosage rates. After selecting best chemical reagents, effect of particle size at selected dosage rates of flotation reagents was studied. The detail of the work is presented as in upcoming section of this paper.

2.3. Flotation reagents

Flotation is a physico-chemical process and its performance or floatability is greatly enhanced using chemical additive or regents (Srdjan, 2007) . Flotation reagents are also used to float selected elements by controlling the surface characteristics of the ores such as hydrophobicity. The most common reagents include: a) collectors to impart hydrophobicity, b) frothers to stabilize the froth, c) depressants to depress the unwanted gangue material, d) regulators to control specific property such as pH and e) activators to change the surface of the mineral chemically .

Three different collectors of anionic types i.e. Xanthates of sulphydryl group (Sodium Amyl Xanthate and Sodium Ethyl Xanthate) and Sulphonate (triton-x-100) of oxyhydryl group were used for flotation of black shale.

Frothers of neutral category including methyl isobutyl carbinol (MIBC) and Pine oil were used. For depressing the gangue material (Clay and silica minerals) sodium silicate was used. The pH was regulated to 9-10 with NaOH.

2.4. Flotation parameters

The various flotation controlling parameters were kept constant throughout the set of experiments and are listed in table 5.

2.5. Floatation process

For floatation, a sample weighing 250g having particle size -212 microns was taken after preparation (collection, crushing. grinding, sieving) and pulp density was set to 33% with 750ml of water. Slurry was then introduced to flotation tester (Denver flotation cell) (Wills, 2006), pH was regulated to the range of 9-10 with NaOH with digital pH meter and impeller was started to agitate the content (pulp). The calculated amount of depressant and collector were added as 10% solution respectively with each conditioning 10 minutes. Finally, frother was added, agitate the pulp for 2-3 minutes and then air supply was started thus forming mineral rich froth as shown in figure 1. The froth was collected for 5-6 minutes and set to filtration to remove water. Then sample was completely dried in oven at 70oC for drying. Dried sample was weighted and analyzed for carbon and metallic content.

To investigate the effects of particle size on floatation response, grounded sample was sieved to four different particle size ranges. Each sample was then subjected to flotation under same flotation parameters such as chemical reagent types, dosage, pH, density of slurry, air flow rate, rpm of flotation machine etc. Floated fraction was then analyzed by loss on ignition test for determination of total carbon content and recovery calculations. It was also examined by XRF and ICP-OES for determining the upgradation of heavy metals entrapped in the carbonaceous content of black shale.

3. Results and discussion

Flotation response of black shale of Chimiari region of Pakistan has been tested and presented in terms of up-gradation of carbonaceous content as well as metal grades. Carbonaceous content is reported as total carbon content (TCC) whereas metal content is reported as base metal by elemental analysis with XRF and ICP-OES. It must be highlighted that the results of XRF are conducted with IQ+ software and exercised as comparative rather than absolute quantitative analysis, which is a technical limitation. The type and dosage of flotation reagents, collectors, frothers and depressants, is selected as follows:

a) Depressant

Sodium silicate (Patrick Zhang, 2008) is tested as depressant of clay minerals and silica at four dosage rates of 0.5, 1.0, 1.5 and 2.0 kg/t from test No.1 to 4 respectively. For all these tests, a dosage rate of 300 g/t of sodium ethyl xanthate as collector and 100 g/t of MIBC as frother are used. Figure 2 shows the results for flotation response at various dosage rates of depressant. Furthermore, it is shown in elemental analyses of table 6, it is observed that 1.5 kg/t of sodium silicate gives best results among the four tests performed and thus subsequently in all test this dosage rate is applied.

b) Collectors:

Three collectors from anionic category are chosen, two of them are the Xanthates (sulphydryl group) and one is sulphonate (oxyhydryl group) i.e. sodium ethyl xanthate, sodium amyl xanthate and triton-x-100 respectively. For xanthate collectors dosage rates of 50, 100, 200 and 300 g/t are used from test no.1 to 4 respectively whereas for triton-x-100 dosage rates are same as that of sodium silicate i.e. 0.5, 1.0, 1.5 and 2.0 kg/t. The caparison of these collectors is presented in figure: 3 and 4 in terms of grades and recovery of TCC. It is inferred that triton-x-100 reports more recovery to float fractions, however, grads are very low. On the other hand, both sodium ethyl xanthate and sodium amyl xanthate gives good recovery with improved grades of TCC. The elemental analyses of XRF (non-normalized) for float fractions are presented in table 7 to 9.

c) Frothers

MIBC (methyl isobutyl carbinol) and pine oil was used as frothers. Both of these chemicals are neutral frothers i.e. their performance is not pH dependent. Results are presented in figure 5 as grade and recovery comparisons at selected dosage rates of 25, 50 and 100 g/t whereas elemental analyses are shown in table 10 and 11. It is concluded that MIBC gives better grade and recovery improvements than pine oil.

To get optimum particle for floatation and to study the effect of particle size, four particle size ranges selected for study include -53, -106+53, -150+106 and -212+150 microns and response of flotation for carbonaceous content

TCC (total carbon content) using loss on ignition and is presented as in figure 6. The floated fraction is analyzed by XRF and ICP-OES to determine the upgradation of heavy metals entrapped in the carbonaceous content of black shale. Table 12 shows the results of elemental analyses of float fraction (XRF) and table 13 presents the chemical analyses conducted by ICP-OES.

Table 4. Chemical analysis of Chmiari black shale.

Elements	Concentration (ppm)
Cu	160
Ni	69
Zn	236
Cr	43
S	48263
Ti	1205
V	524

Table 5. Floatation parameters.

Parameter name	Value
pH	9-10
Pulp density	33%
Air Flow	50-60%
Machine RPM	1500 rpm
Grain size (other than specified)	-212 microns
Conditioning time	10 min
Flotation time	5-6 min

Table 6. Elemental analysis of float fraction using four different dosage rates of depressant.

Element	Concentrate grades (%)				
	Dosage rate (g/t)				
	Feed	0.5	1.0	1.5	2.0
Cu	0.041	0.033	0.194	0.210	0.184
Ni	0.025	0.008	0.031	0.010	0.007
Zn	0.024	0.514	0.317	0.229	0.227
Cr	0.043	ND	0.044	0.042	ND
S	0.677	3.422	0.748	0.581	0.542
Ti	0.459	0.531	0.447	0.454	0.475
V	0.184	0.227	0.196	0.191	0.208

Table.7. Elemental analysis of float fraction using four different dosage rates of Triton-X-100 collector.

Element	Concentrate grades (%)				
	Dosage rate (g/t)				
	Feed	0.5	1.0	1.5	2.0
Cu	0.041	0.169	0.160	0.160	0.031
Ni	0.025	0.019	ND	0.012	0.028
Zn	0.024	0.269	0.241	0.227	0.247
Cr	0.043	0.035	0.030	ND	0.034
S	0.677	0.195	0.208	0.214	0.206
Ti	0.459	0.405	0.410	0.413	0.441
V	0.184	0.167	0.169	0.163	0.169

Table 8. Elemental analysis of float fraction using four different dosage rates of sodium ethyl xanthate collector.

Element	Concentrate grades (%)				
	Dosage rate (g/t)				
	Feed	50	100	200	300
Cu	0.041	0.208	0.245	0.213	0.190
Ni	0.025	0.004	0.023	0.014	0.012
Zn	0.024	0.245	0.254	0.228	0.237
Cr	0.043	0.034	0.026	0.037	0.042
S	0.677	0.290	0.137	0.356	0.324
Ti	0.459	0.509	0.500	0.441	0.460
V	0.184	0.207	0.200	0.167	0.182

Table 9. Elemental analysis of float fraction using four different dosage rates of sodium amyl xanthate collector.

Element	Concentrate grades (%)				
	Dosage rate (g/t)				
	Feed	50	100	200	300
Cu	0.041	0.204	0.049	0.160	0.034
Ni	0.025	0.015	0.013	0.008	0.013
Zn	0.024	0.344	0.132	0.203	0.209
Cr	0.043	0.025	0.028	0.041	ND
S	0.677	0.370	0.200	0.441	1.255
Ti	0.459	0.576	0.547	0.466	0.572
V	0.184	0.227	0.225	0.189	0.230

Table 10. Elemental analysis of float fraction using three different dosage rates of MIBC frother.

Element	Concentrate grades (%)			
	Dosage rate (g/t)			
	Feed	50	50	100
Cu	0.041	0.039	0.051	0.045
Ni	0.025	0.013	0.021	0.017
Zn	0.024	0.218	0.242	0.221
Cr	0.043	0.047	0.017	0.048
S	0.677	0.682	0.316	0.261
Ti	0.459	0.621	0.602	0.571
V	0.184	0.224	0.222	0.216

Table 11. Elemental analysis of float fraction using three different dosage rates of Pine oil frother.

Element	Concentrate grades (%)			
	Dosage rate (g/t)			
	Feed	50	50	100
Cu	0.041	0.046	0.157	0.238
Ni	0.025	ND	0.020	ND
Zn	0.024	0.234	0.237	0.217
Cr	0.043	0.044	0.041	ND
S	0.677	0.254	0.267	0.274
Ti	0.459	0.577	0.505	0.459
V	0.184	0.209	0.180	0.184

Fig. 1. Froth collection and drying process.

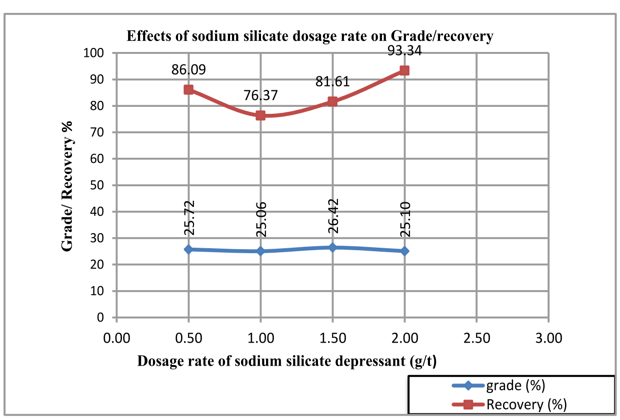

Fig. 2. Effect of sodium silicate dosage on grade and recovery of TCC.

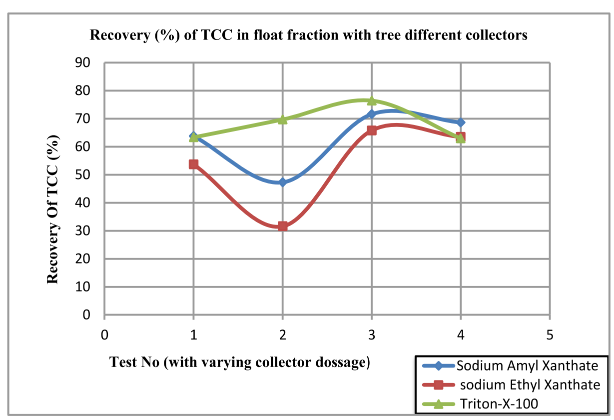

Fig. 3. Recovery of TCC with the three collectors.

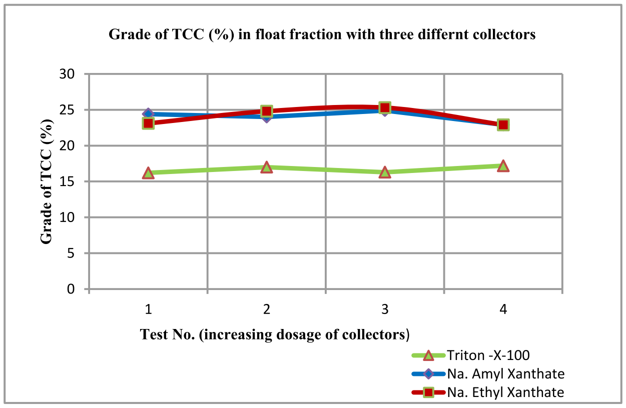

Fig. 4. Grade of TCC (%) in float with three different collectors.

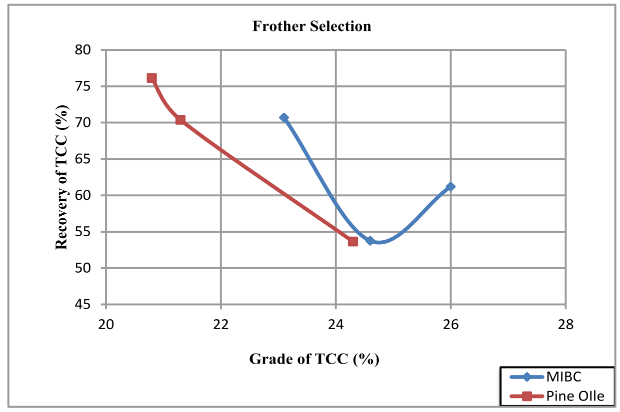

Fig. 5. Grades – recovery comparison of MIBC of Pine oil.

Table 12. Elemental analysis of float fraction (using XRF).

Element	Concentrate grades (%)				
	Particle Size (microns)				
	Feed	-53	-106+53	-150+106	-212+150
Cu	0.041	0.060	0.041	0.023	0.031
Ni	0.025	0.020	0.014	0.021	0.011
Zn	0.024	0.278	0.401	0.253	0.285
Cr	0.043	0.043	ND	ND	0.045
S	0.677	1.161	0.220	0.209	0.231
Ti	0.459	0.634	0.597	0.488	0.554
V	0.184	0.215	0.232	0.187	0.235

Table 13. Chemical analysis of float fraction (using ICP-OES).

Element	Feed grades (ppm)				
	Particle Size (microns)				
	Feed	-53	-106+53	-150+106	-212+150
Cu	160	237	160	237	160
Ni	69	59	69	59	69
Zn	236	271	236	271	236
Cr	43	55	43	55	43
S	48263	25258	48263	25258	48263
Ti	1205	1703	1205	1703	1205
V	524	604	524	604	524

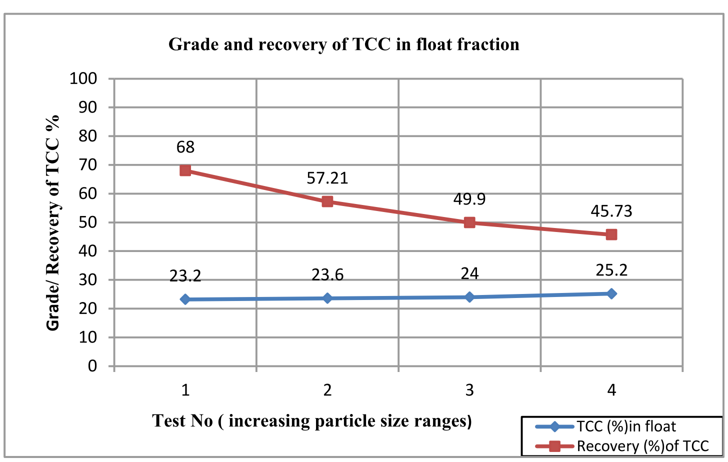

Fig. 6. Grade and recovery at four particle sizes.

4. Conclusions

The carbonaceous content (TCC) of sample of black shale from Chimiari region of Khyber Pakhtunkhwa Pakistan is upgraded from 15.8% in sample to about 25% in the float fraction and best results are obtained with xanthate collectors both in terms of grade and recovery improvements. It is observed that Sodium silicate depresses clay, calcite and silica minerals however complex silicates are not depressed with it. Depressing efficiency also decreases when collector is added.

Triton-X-100 gives highest recoveries among three collectors however, grades are not improved. Sodium ethyl xanthate gives more improved results for Cu, Zn, Ti and V etc. than sodium amyl xanthate. Keeping in view the grade –recovery aspect of TCC, it is observed that a dosage rate of 200 g/t of sodium amyl xanthate give better results than triton-x-100 or sodium ethyl xanthate.

MIBC is found a better frother than pine oil both in terms of grads and recoveries of carbon (TCC) and metals.

It is observed from particle size analyses that fine grinding improves recovery of TCC from 45% at -212+150 micron to 68% at -53 microns conversely, grads are decreased. It is also found that fine grinding also improves recovery of heavy metals.

Author's contribution

Muhammad Tahir, Zahid Ur Rehman and Sajjad Hussain, proposed the main concept, involved in write up and did provision of relevant literature, and review and proof read of the manuscript. Muhammad Nazir, assisted in establishing sequence stratigraphy of the section. Muhammad sadiq, collected field data. Noor Mohammad and Iltaf Hussain did technical review before submission and proof read of the manuscript

References

Barry A. Wills, 2006. Mineral Processing Technology, An Introduction to the Practical Aspect of Ore Treatment and Minerals Recovery (Vol. 7th Edition).

Bhatti , M. T., Shafiq, M., Aziz, A., Iqbal, M. M., 2013. Mineral Evaluation of Black Shale of Chimiari region of Khyber Pakthunkhawa, Pakistan by Size Analysis. International Journal of Engineering & Technology, 13, 61-68.

Bhatti, M. T., Butt, K. A., 2007. Bioleaching of Uranium from Chimiari low -grade bleck shale ores. AEMC, Lahore.

Bhutti, M. T., Aziz, A., Shafiq, M., Sajjad, M., Iqbal, M. M., Muhammad, B., 2013. Characterization of black shale Chimiari Khyber Pakhtunkhwa region of Pakistan for its potential as multi-mineral. International Journal of Scientific Research, 2, 231-238.

Das, A., Rao, K. H., Sharma , P. K., Natarajan, K. A., Forssberg, K. S., 1999. Sarface Chemical Adsorption Studies using Thiobacitllus Ferroxidants with Reference to Bacterial Adhesion to Sulfide Minerals. International Biohydrometallurgy Symposium (IBS), 97-708.

International Atomic Energy Agency (IAEA), 1993. Uranium Exraction Technology, Technical Report Series No. 359. Vienna: IAEA.

International Atomic Energy Agency (IAEA), 2009. World distributuions of uranium deposits (UDEPO) with uranium deposit classification. Vienna: IAEA-TECDOC-1629.

James, T., 1998. Patent No. 4719009.

Langwaldt, J., Kalapudas, R., 2007. Bio-Benfication of Multimineral Black Shale Ore by Flotation. Physicochemical Problems of Mineral Processing, 41, 291-299.

Loukola Ruskeeniemi, K., Heino , T., 1996. Geochemistry and Gensis of the Black Shale - Hosted Ni-Cu-Zn Deposits at Talvivaara, Finland. Economic Geology, 91, 80-110.

Patrick Zhang., 2008. An investigation of Floatation Reagents. Florida, USA: Florida Institute of Phosphate Research (FIPR).

Santhiya, D., Subramanian, S., Natrajan, K., hunumantha, R. K., Forssberg, K., 2001. Biomodulation of Galena and Sphalerite Surfaces using Thiobacillus. International Journal of Mineral Proccesing, 62, 121-141.

Sharma, P. K., 2001. Surface Studies Relevant to

Microbial Adhesion and Bioflotation of Sulphide, PhD Thesis. University of Lulea, Sweden. Unpublished, 330-334.

Smith, R. W., Miettnen, M., 2006. Microorganisms in flotation and flocculation: Future technology or laboratory curiosity? Minerals Engineering, 19, 548-553.

Smith, R. W., Misra, M., Chen, S., 1993. Adsorption of a hydrophobic bacterium onto hematite: implications in the froth flotation of the mineral,. J. Ind. Microbiol, 11, 63-67.

Srdjan M, B., 2007. Handbook of Floatation Reagents, Chemistry, Theory and Practice, Sulphide Ores. Elsevier.

Vernon , E. S., 1961. Geology and geochemistry of uranium in marine black shale a review. Reston, VA: U.S. Geological Survey.