

## Chemical Extraction of Copper from Copper Sulphide Ores of Pakistan by Roast Leach Method

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**Abstract.** Copper ores, containing both complex sulphide minerals and those containing chalcopyrite mineral, were studied for the extraction of copper by leaching after roasting. Roasting at 650 °C for 30 min rendered the ore leachable in dilute sulphuric acid of 2.5% concentration. The process of metal extraction would be of hydrometallurgical importance for low to high grade sulphide and polymetallic complex sulphide ores occurring in Pakistan. The kinetic models of roasting reaction fit phase boundary as well as diffusion reaction mechanism.

**Keywords:** copper sulphide, copper hydrometallurgy, polymetallic ores, ore roast-leach method

### Introduction

Major occurrence of sulphide ores in Pakistan and elsewhere is of two genetic types related to subduction and partial melting of mafic magma under Eurasian plate producing calc alkaline magmatism (Sillitoe, 1972). The major copper mining in Baluchistan is of Saindak porphyry copper ore which contains chalcopyrite and pyrite minerals. In Dir and Chitral areas, the primary hypogene chalcopyrite and sphalerite assemblage has given rise to supergene epithermal assemblage of tetrahedrite, chalcocite, sphalerite, galena and/or chalcopyrite. The potassic and phyllitic zones and hydrothermal alterations have caused such changes in mineralogy (Tahirkheli *et al.*, 2005).

The sulphide minerals of copper are not easily leached (Davenport *et al.*, 2002) and require high pressure and temperature for leaching or prior treatment to decompose sulphide minerals. The methods for the copper extraction from such refractory copper sulphide ores range from pretreatment of the ores by oxidative roasting, autoclave oxidation or bio-oxidation, chloride leaching, sulphate leaching and chloride-sulphate leaching. The oxidation roast leaching is now termed as the first choice followed secondly by the temperature pressure leaching (Prasad and Pandey, 1998).

In this study prior roasting of indigenous copper ore samples from Chitral and Saindak were conducted. Previously, Rani *et al.* (1998) studied leaching parameters such as temperature, pressure, oxidizing agent and acid concentration. The result showed that acid leaching of copper sulphide ores requires nitric acid leaching under pressure and temperatures.

Roasting prior to leaching was carried out in the present work mainly on indigenous copper sulphide ores. It was shown that without roasting or pretreatment, chalcopyrite presents problems (Padilla *et al.*, 2003) related to great resistance of this mineral during leaching. It was thought that pretreatment by roasting of copper sulphide ores and chalcopyrite concentrate would transform its mineralogy and make it amenable to leaching. The roasting parameters, such as temperature and roasting time, were optimized in the present study. The leaching parameters such as leaching time, acid concentration and solid liquid ratio during subsequent leaching were also studied. No work has been reported previously on the roast-leach processing of complex sulphides ores and the mechanism of reaction.

### Materials and Methods

**Sampling and comminution studies.** Bulk ore samples of copper ore containing complex sulphide ores, collected from Kaldam Gol area at Darosh in Chitral, (35° 32' 59" N, 71° 48' 16.30" E) and copper sulphide (chalcopyrite concentrate) of Saindak area, Baluchistan (29° 14' 00" N, 61° 36' 49.5" E), were procured under University of Education, HEC Project No. 870. The Darosh samples (C) were taken from the ore dump at the exploratory mines representing different areas of copper deposits. Mine samples were collected after detailed geochemical exploratory survey of Darosh area. Concentrate of Saindak copper ore (sample E) from Baluchistan was prepared by flotation.

Samples were prepared by first crushing in a jaw crusher with an opening of one inch size. The crushed material was later ground to ¼ inch size by roll mill. The material was quartered by riffle. A portion of quartered material was passed through

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disc grinder. One half of disc grinded material was pulverised by Tema mill, up to the size of -300 to -400 mesh. Other half was passed through different sieve sizes of 50, 100, 200, 250 and 300 mesh. The samples passing 300 mesh size were used for different types of instrumental, mineralogical, physical and chemical analyses. Different mesh sizes were examined by Reichert ore microscope.

**Dissolution of ore samples.** Ore samples were completely dissolved by using HF and perchloric acid. The chemical constituents were analysed using standard analytical methods (Vogel and Bassette, 1961) and atomic absorption spectrophotometry using Thermo Fisher Solaar Model iCE3300L.

**Roasting of ore samples.** The roasting herein refers to heating the copper sulphide ore in a furnace at specific temperature. Powdered ore passing 300 mesh size was taken in a china crucible. The covered crucible was placed in muffle furnace for roasting at different temperatures ranging from 500 °C to 800 °C. The roasting time was varied from 30 min to 240 min. The pulverized copper ore samples marked as C (complex copper sulphide) and E (chalcopyrite) were heated at different temperatures for varied time periods. Sample in a covered crucible was heated in a muffle furnace for 3 h. When the temperature reached 500 °C, the crucible was placed in a desiccator for cooling. The roasted material was ground in pestle and mortar for leaching studies. The amount of leached copper was determined by standard analytical methods. The same procedure was repeated for temperatures of 550 °C, 600 °C, 650 °C, 700 °C, 750 °C and 800 °C. Roasting parameters such as roasting time and temperature and particle size of ore were investigated. Leaching parameters such as leaching time, acid concentration and solid-liquid ratio were also studied on roasted ore samples.

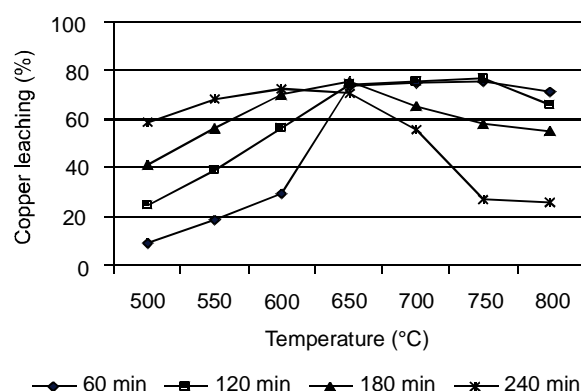
**Leaching of roasted copper ores using sulphuric acid.** The leaching tests were carried out in a Pyrex beaker with sulphuric acid of known strength. The slurry was agitated with a glass stirrer and sample was drawn with a pipette attached with a porous plug, after 2, 5, 10, 20 and 30 min agitation and preserved for subsequent analysis. The weighed roasted material was leached with 2.5 percent  $H_2SO_4$  by using 1:5 solid liquid ratio. The samples were analysed using standard analytical methods (Vogel and Bassette, 1961). All the leaching tests were carried out at room temperature (35 °C).

## Results and Discussion

The ore samples were found to contain different base metals. Sample C contained 21.13% copper, 1.72% zinc, 2.14% iron, 0.06% lead, 3.15 ppm silver and 1.09 ppm gold. Sample E

(chalcopyrite concentrate of Saindak) contained 26.17% copper, 23.78% iron and traces of gold. Microscopic study and XRD analysis of sample C showed the presence of chalcopyrite, chalcocite, azurite, tetrahedrite and malachite as copper minerals. The treated samples indicate the formation of oxides and sulphates of copper. The sample E contained mainly chalcopyrite with subordinate amounts of pyrite.

The experiments showed that the leachability (the amount of copper leached in a sample by sulphuric acid solutions) of complex copper sulphide ore (sample C) increased with increase in roasting time even after roasting at lower temperature in the range of 500 °C to 650 °C. Leaching of copper was 73% with 60 min roasting at 650 °C but 70% copper was leached after roasting for 180 min at 600 °C. When the temperature was raised from 650 °C to 800 °C, the leachability of sample C was maximum with increase in temperature using 120 min roasting time. However, further increase in roasting time beyond 120 min decreased the leachability. The results are illustrated in Fig. 1. Maximum leaching of copper from complex copper sulphides ore (sample C) was achieved at 650 °C after 60 min roasting.



**Fig. 1.** Effect of roasting temperature on copper leaching in sample 'C'.

**Effect of roasting time on copper leaching at optimum temperature.** Sample C was roasted at 650 °C for time periods of 30, 60, 120, 180, and 240 min. The results indicated that optimum extraction of copper was achieved in 30 min by simple roasting. After 30 min, no significant difference in extraction of copper was found. Extraction of copper remained constant after 30 min roasting time. The results are presented in Table 1.

**Effect of leaching time on leaching of simple roasted ore.** The roasted sample C was leached with 2.5% sulphuric acid solution with 1: 5 solid liquid ratio for different time periods

i.e., 15, 30, 120, 900, 1800 and 3600 sec. Optimum amount of copper extracted was 73% in only 30 sec. It was shown that the maximum leaching of the complex copper sulphides ore (sample C) occurred in 30 sec., using very dilute sulphuric acid. The results are shown in Table 2.

**Table 1.** Effect of roasting time on copper leaching at optimum temperature

Roasting time (min.)	Copper leaching (%)
30	72.85
60	73.40
120	74.25
180	75.43
240	70.36

Sample C: optimum roasting temperature = 650 °C; particle size = 300 mesh; leachant = 2.5% H<sub>2</sub>SO<sub>4</sub>; solid liquid ratio = 1:5; leaching time = 02 min.

**Table 2.** Effect of leaching time on leaching of simple roasted ore

Leaching time (s)	Copper leaching (%)
15	70.30
30	72.55
120	72.85
900	73.35
1800	74.75
3600	76.10

Roasted sample C at 650 °C; roasting time = 30 min; leachant = 2.5% H<sub>2</sub>SO<sub>4</sub>; particle size = 300 mesh; solid liquid ratio = 1:5.

**Effect of sulphuric acid concentration on leaching of roasted ore.** To observe the leaching behaviour of roasted ore, sample C was treated after roasting with different concentrations of sulphuric acid i.e., 0.5, 1.25, 2.5, 5 and 10%. It was observed that the rate of dissolution of roasted complex copper sulphide ore increased with increase in the acid concentration. Acid strength higher than 5.0% did not show significant increase in the copper extraction. It is apparent from the results that maximum copper leached within 2 min using even 2.5% sulphuric acid. However, the leaching rate became almost constant when the leaching was carried out with an acid concentration higher than 2.5%.

**Effect of solid liquid ratio on leaching of roasted ore.** A series of experiments were conducted using copper complex sulphide ores of 300 mesh size. The results indicated that the extraction of copper was 49% at solid liquid ratio of 1:2.5. Further increase of solid liquid ratio from 1: 5, yielded only a

slight increase in copper extraction. From the leaching of copper it was evident that a solid liquid ratio of 1:5 offered a workable operating condition for simple roasted material at which 73% copper extraction was achieved.

**Effect of particle size on leaching of roasted ore.** A number of tests were performed to find out the particle size range, which gave maximum copper extraction. Complex copper sulphide ore was pulverized to obtain samples passing through 100, 150, 200 and 300 mesh sieves. Finer particle of size -300 mesh showed optimum extraction of copper from roasted material; with further decrease in size, copper extraction became constant.

**Leaching of copper chalcopyrite concentrate.** Detailed study of simple roasting of complex copper sulphide ore was also conducted on the sample of copper chalcopyrite concentrate. The results obtained are presented in Table 3, showing increase in leaching of copper with increase in temperature.

**Table 3.** Leaching of copper chalcopyrite concentrate (sample E)

Roasting time	Roasting temp.	Copper leaching (%)
3 h	500 °C.	39.79%
3 h	550 °C	45.44%
3 h	600 °C	64.65%
3 h	650 °C	69.85%
30 min	650 °C	70.47%

Leachant = 2.5% H<sub>2</sub>SO<sub>4</sub>; leaching time = 02 min; solid liquid ratio = 1: 5.

**Kinetic and thermodynamic studies.** Kinetic models were used to determine the reaction rate and calculate the activation energies and the thermodynamic parameters of the reactions. The kinetic model (Sharp *et al.*, 1966) was compared with the present experimental results to investigate the mechanism of reactions, using diagnostic equation. The activation energy was calculated with the Arrhenius expression:

$$K = A e^{-E_a/RT}$$

$$\ln K = \ln A - E/RT$$

where:

K is the rate coefficient,

A is the frequency factor,

R is the gas constant,

T is the absolute temperature and

E<sub>a</sub> is the activation energy evaluated from the slope of the Arrhenius lines.

The results (Table 4) suggest that the reactions mechanism during the roasting has phase boundary reaction as well as diffusion reaction.

**Table 4.** Comparison of activation energy using different kinetic models

	Activation energy									
	D1	D2	D3	D4	F1	A2	A3	R2	R3	
Simple roasting of sample C	73	80	87	82	59	33	23	52	54	

The mechanism of roasting reactions was determined by the computation of experimental data using equations of Sharp's kinetic models. The mechanism of solid state reactions was determined using diagnostic equation as follows:

$$\ln[-\ln(1-\alpha)] = m \ln t + \ln B$$

The value of  $m$  was obtained by slope, when the  $\ln[-\ln(1-\alpha)]$  was plotted vs  $\ln t$ . The experimental data can be analysed using a 'diagnostic equation' of general use (Sharp *et al.*, 1966). Where  $\alpha$  is the recovery (fraction reacted at time  $t$ ),  $t$  is time,  $B$  is a constant which depends in part on the nucleation frequency and linear rate of grain growth,  $m$  is a constant that can vary according to the geometry of the system. The characteristics established empirically are between 0.53 and 0.58 for diffusion limited equations, 1.07 and 1.11 for the phase boundary reaction models and 2.00 and 3.00 for the nucleation models (Hancock and Sharp, 1972).

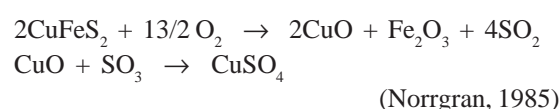
**Reaction mechanism for simple roasting of copper sulphide ore.** Value of  $m$  ranges from 1.63 to 0.64 at lower temperature range of 500 °C to 600 °C. When temperature goes higher from 600 °C to 800 °C, the values of  $m$  become less than zero. The mechanism of roasting reaction is from phase boundary to diffusion area at lower temperature range. Value of  $m$  are given below:

Temperature:	500 °C	550 °C	600 °C	650 °C
	700 °C	750 °C	800 °C	
Value of $m$ :	1.63	1.25	0.64	-0.032
	-0.37	-0.95	-0.89	

The results in this work verified mineralogical studies of Evrard (2001) that the chalcopryrite decomposed due to the formation of discrete particles of  $\text{Cu}_2\text{S}$  with a size-range from 5 to 20 or more micrometers by controlled desulphurisation process at relative low temperatures (650 °C). During roasting the changes in chemistry of chalcopryrite is shown by X-ray

studies (Deer *et al.*, 1962-1963). When heating without controlled sulphur pressure, the chalcopryrite passes into a high temperature phase at 550 °C. This shows that the heat treatment of chalcopryrite should be less than 550 °C for deformation of structure. Deer *et al.* (1962-1963) stated that when chalcopryrite is heated in air, it shows an exothermic DTA peak at 500 °C.

Sulphide minerals are converted into water soluble sulphates by roasting through the mechanism of converting sulphides to sulphates which proceeds *via* an oxide as follows:



Different routes in hydrometallurgical techniques employing prior roasting before leaching of copper sulphide ores are roasting at high temperatures (Mulaba-Bafubiandi and Waanders, 2005), roasting with elemental sulphur (Padilla *et al.*, 2003) and with sulphur dioxide and oxygen (Jaquay, 1979; Frankewicz, 1978; Huggins *et al.*, 1977; Turkdogan and Rice, 1974). The other example is chlorination during roasting with salts or gas (Kanari *et al.*, 2001; Dubrovsky and Marcantonio, 1992; Agnew, 1976). In some processes sulphatisation and chlorination were carried out simultaneously during the roasting process (Frankewicz, 1978; Lippert and Kudelka, 1976). Some of the non-polluting hydrometallurgical processes are based on sulphatising the copper sulphide complex ores or concentrates (Minic *et al.*, 2005; Norrgran, 1985).

Copper sulphide minerals formed oxides or sulphates on roasting and sulphur dioxide is released (Davenport *et al.*, 2002). The oxides formed are readily leachable in sulphuric acid solutions and the sulphates are leachable in water. These changes may occur at temperature range 500 °C to 650 °C but when the temperature is raised above 650 °C extraction of copper decreased. It may be due to the formation of new species of minerals, which resist leaching (Evrard, 2001). There may be intermediate minerals or solid solutions formed on prolonged heating which are difficult to leach.

**XRD analysis.** XRD analyses of selected samples were carried out. The XRD analysis of sample C showed the presence of chalcopryrite, chalcocite, azurite, tetrahedrite and malachite as copper minerals. The treated sample shows the formation of oxides and sulphate of copper after roasting for 30 min. The XRD analyses are interpreted in Figs. 2-3.

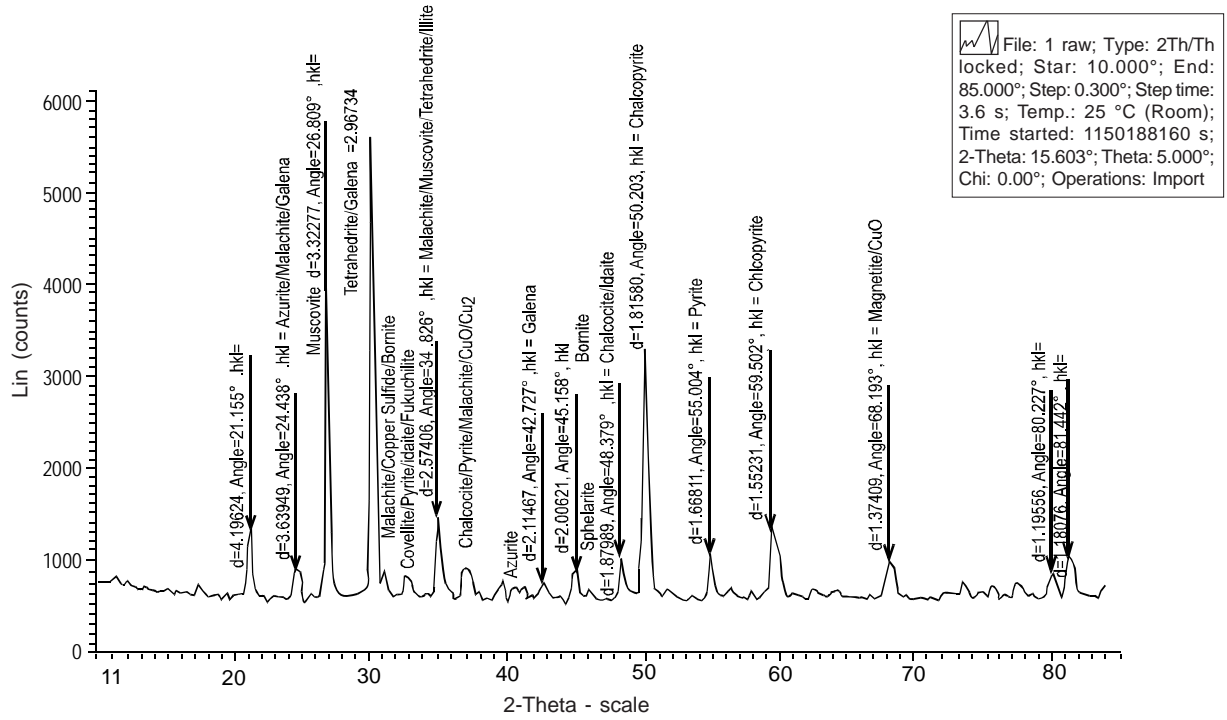


Fig. 2. XRD image of copper ore (sample C).

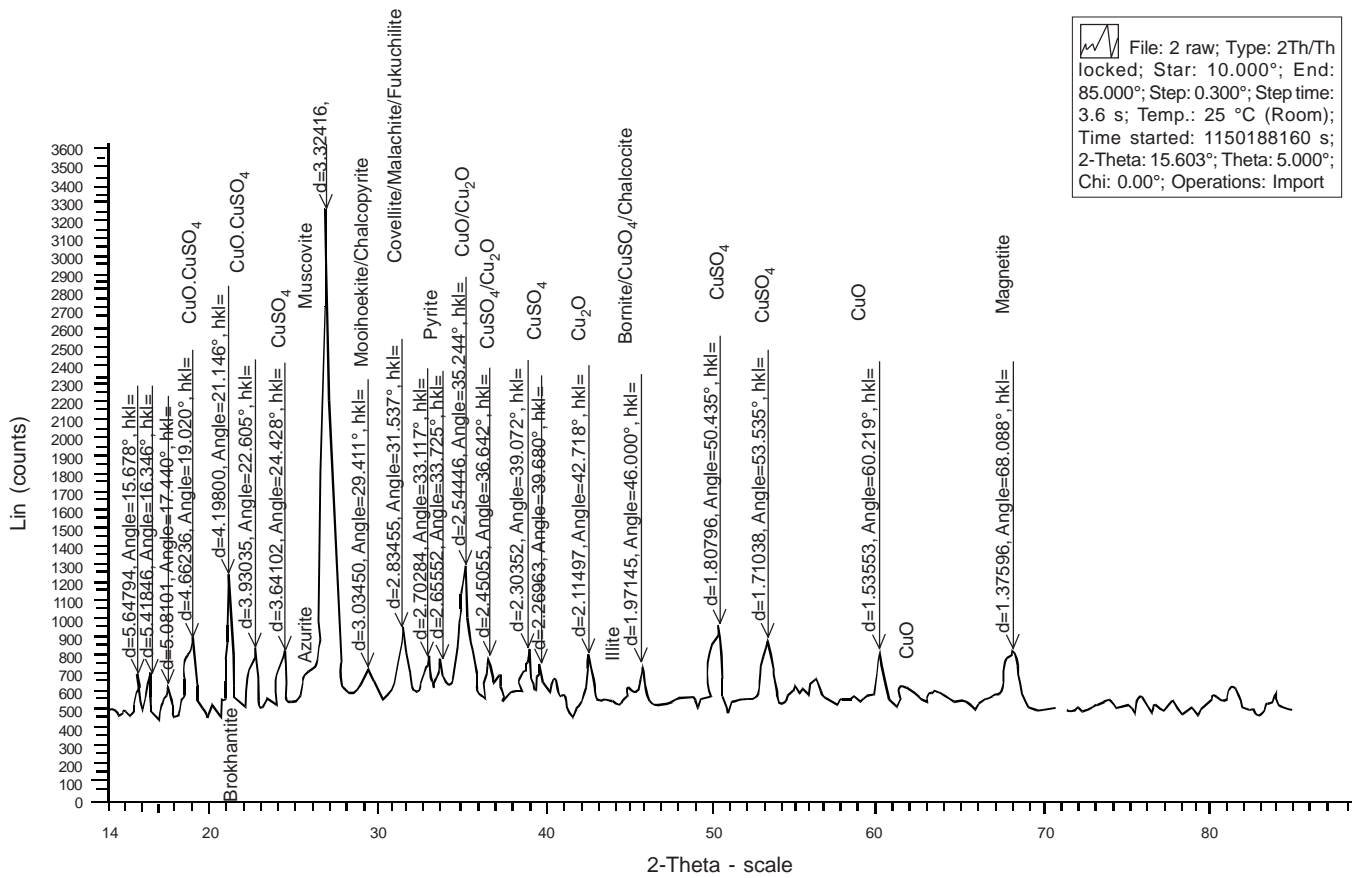


Fig. 3. XRD of simple roasting of sample for 3 min. at 650 °C.



## Conclusion

It is concluded that the copper sulphide ores containing chalcopyrite and complex sulphide mineral are not leached easily. A suitable and cheap method to leach the sulphide copper containing chalcopyrite ore as well as complex sulphide ore for the economic utilization is developed by roasting studies in this paper. The optimum copper leaching achieved by prior roasting was 70 to 75%. The work on roasting and leaching of complex sulphide and reaction mechanism was not conducted previously. Small deposits of low grade ores and poly-metallic or multi-element indigenous ores can be utilized by this chemical process. The work would be extended to gold silver ores, treatment of which poses environmental problems using conventional cyanidation technique.

## References

- Agnew, K.L. 1976. Iron Chloride Activated Oxidation of Sulfide Ores. US Patent No: 3, 981, 963, 21<sup>st</sup> November, 1976.
- Davenport, W.G., King, M., Schesinger, M. Biswas, A.K. 2002. *Extractive Metallurgy of Copper*, 460 pp., 4<sup>th</sup> edition, Elsevier Science Ltd., Oxford, U.K. ( 1<sup>st</sup> edition in 1975).
- Deer, W.A., Howie, R.A., Zussman, J. 1962-1963. *Rock Forming Minerals*, 5 volumes, 528 pp., Longmans, London, UK.
- Dubrovsky, M., Marcantonio, P.J. 1992. Process for Recovering Metals from Refractory Ores. US Patent No. 5, 104, 445, 4<sup>th</sup> April, 1992.
- Evrard, L.J. 2001. The mineralogical transformation of a polymetallic sulfide ore during partial roasting. *Journal of Metals*, **53**: 42-44.
- Frankewicz, T.C. 1978. Selective Sulfation Process for Partitioning Ferrous and Non-ferrous Values in an Ore. US Patent No. 4, 110, 106, 29<sup>th</sup> August, 1978.
- Hancock, J.D., Sharp, J.H. 1972. Method of comparing solid-state kinetic data and its application to the decomposition of kaolinite, brucite and BaCO<sub>3</sub>. *Journal of the American Ceramic Society*, **55**: 74-77.
- Huggins, D.K., Anderson, L.R., Gefri, F.J. 1977. Recovery of Copper from Copper Sulfide Ores Containing Copper and Iron. US Patent No. 4,003,740, 18<sup>th</sup> January, 1977.
- Jaquay, L.H. 1979. Process for Converting Non-ferrous Metal Sulfides. US Patent No. 4, 155, 749, 22<sup>nd</sup> May, 1979.
- Kanari, N., Gaballah, I., Allain, E. 2001. A low temperature chlorination-volatilization process for the treatment of chalcopyrite concentrates. *Thermochimica Acta*, **373**: 75-93.
- Lippert, K., Kudelka, H. 1976. Combined Process for Working up Pure and Complex Copper Concentrates. US Patent No.3, 969, 107, 13<sup>th</sup> July, 1976.
- Minic, D., Strbac, N., Mihajlovic, I., Petkovic, D., Zivkovic, Z. 2005. Kinetic parameters for the process of sulfatization roasting and leaching of copper-lead matte. *Scandinavian Journal of Metallurgy*, **34**: 250-255.
- Mulaba-Bafubiandi, A., Waanders, F. 2005. Hydrometallurgical extraction of Zinc and Copper - A57 Fe-Mossbauer and XRD approach. *Hyperfine Interactions*, **161**: 33-42.
- Norrgran, D.A. 1985. Processes for Sulfatization of Non-ferrous Metal Sulfides. US Patent No.4, 541, 993, 17<sup>th</sup> September, 1985.
- Padilla, R., Rodriguez, M., Ruiz, M. C. 2003. Sulfidation of chalcopyrite with elemental sulfur. *Metallurgical and Materials Transactions B*, **34**: 15-23.
- Prasad, S., Pandey, B.D. 1998. Alternative processes for treatment of chalcopyrite - A review. *Mineral Engineering*, **11**: 763-781.
- Rani, F., Khan, I.H., Mahamood, F., Iqbal, M.Z. 1998. Studies on the leaching of copper from complex copper ores of Chitral mineral and metals. *Pakistan Journal of Scientific and Industrial Research*, **41**: 139-143.
- Sharp, J.H., Brindley, G.W., Achar, B.N.N. 1966. Numerical data for some commonly used solid state reaction equations. *Journal of the American Ceramic Society*, **49**: 379-382.
- Sillitoe, R.H. 1972. A plate tectonic model for the origin of porphyry copper deposits. *Economic Geology*, **67**: 184-197.
- Tahirkheli, T., Khan, M.A., Shah, M.T. 2005. Geochemistry and petrogenesis of metavolcanic rocks in Gawuch and Drosh formations, Chitral, northern Pakistan. *Geological Bulletin of University of Peshawar*, **38**: 189-202.
- Turkdogan, E.T., Rice, B.B. 1974. Copper Recovery from Lean Sulfide Ores. US Patent No. 3, 839, 013, 1<sup>st</sup> October, 1974.
- Vogel, A.I., Bassett, J. 1961. *Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, 3<sup>rd</sup> edition, English Language Book Society and Longmans Green and Co. Ltd., London, UK.