Industrial Exploitation of Pyrite

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Pyrite is the most common and wide spread of sulphides. It gets depostied at both high and low temperatue. It occurs, as direct magnetic and as an accessory mineral in igneous rocks, also in contact metamorphic and hydrothermal vein deposits. Pyrite is a common mineral in sedimentary rocks being both primary and secondary in origin. It is also associated with many minerals but found most frequently with chalcopyrite, sphalerite and galena.

Pyrite occurs in crystals or aggregates of crystals and frequently in fine or granular masses and also in stalactites. It is brittle and has a metallic luster usually harder than other metallic sulphides; specific gravity 4.78. The colour on fresh surface is nearly uniform pale brass-yellow and the streak in greenish black and brownish black. It gets on exposure to atmosphere into iron sulphate or to the hydrated oxide called limonite. The gangue includes carbonates, argillaceous and carbonaceous materials. Two types of pyrite are noted; discrete idiomorphic crystals occur mainly as clusters, and disseminated in a cryptocrystal pyritic base. The idiomorphic crystals are octahedral. Ward[2] studied three types of pyrite, hard, soft and breccia in the pyrite body, which represent the effect of replacement of different beds of limestone. Supergene and hydrogene copper ore bodies in the pyrite body are localized by chemical lighological and structural factors. Dzhafarou[3] determined the effect of impurities on the crystal habit and the lattice parameters of pyrite by a study of different number of pyrite crystals from various sources in U.S.S.R., England and Finland. Pyrite crystals contained various amounts or none of the following admixture, Si, Al, Mg, Pb, Bi, Cu, Ag, Au, Zn, Ca, Co, Mn, Cr, Ni, or no Co. Crystals of pentagonal dodecahedral habit have 0.04-0.05%, Co, while those of octahedral habit contain 0.4%.

Large and extensively developed deposits occur at Rio Tinto in Spain and also in Portugal. Big deposits of pyrite in U.S.A. are Prince William, Louisa, Pulaski and Virgina. Until ecently, the annual world production of pyrite was about 7 million tons, which came mainly from U.S.A., Spain, Japan, Canada, Italy, Cyprus, Portugal, France, Australia and Greece.

In Pakistan, pyrite is reported[4,5] in large quantities forming saddle reefs in large folded limestone and combined with magnetite and copper ores and also in quartz veins as gangue minerals often associated with galena, cuprite and tetrahedrite in Baluchistan and N.W.F. provinces. Sizeable deposits of high grade pyrite have been discovered by Farooqi[6] in Reshian Valley, Azad Kashmir, but the area is surrounded by high mountains covered with quite thick forest. The hight above sea level is 7200 ft.

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Pyrite is a disulphide of iron, FeS_2 containing large percentage of iron and sulphur. It may also contain small amounts of nickel and cobalt and frequently carries minute quantities of gold and copper. Pyrite is easily altered into oxides of iron usually limonite. Samples of massive-vein type pyrite from Reshian, Azad Kashmir were analysed[7] and found to be rich in S 34.77 – 53.35, Fe 45.24 – 3.23 and Al 0.44 – 1.51%. Pyrite and pyrrhotite are the principal deposits in Rajasthan, India, the pyrite contains As 50 – 250, Ni 8 – 60, Co < 10 – 30, Pb 60 – 100, V4 – 6 & Au 0.8-4 ppm; the deposits are of hydrothermal origin[8], Ghosh[9] analysed by emission spectroscopy the minor elements in the pyrite ore of Bihar, India, and found Co 0.076 - 0.36, Ni 0.062 - 0.15, Ag 0.0011 – 0.0035, Mn 0.0044 – 0.02, Ti 0.0053 – 0.061, Bi < 0.0015 - 0.011 and Mo < 0.003 - 0.0096%.

Most deposits of the world are chiefly used to furnish suphur for sulpuric acid. It is roasted in many different types of furnances to yield sulphur dioxide which is also used in the manufacture of sulphuric acid. Robson[10] compared hearth furnances, rotary kilns, flush roasters and fluidized roasters for pyrites roasting operations and described their advantages and disadvantages. The gas SO_2 is used extensively in the preparation of wood pulp for manufacturing of paper. Dorenfeldt[11] gave a general discussion

about the use of pyrite in the making of sulphite liquor, with particular reference to Herreshoff burner. In Canada, a pulp manufacturing company[12] used the pyrite to get sulphur dioxide. Pure SO_2 can be economically produced[13] from pyrite at optimum temperature at 800°.

Elemenal sulphur is also being economically obtained from pyrite. Hall[14] described a method for producing sulphur from pyrite by subjecting the material at 700 – 900° to a reducing flame and distilling off the free sulphur. Rowe[15] described a process for extracting sulphur from pyrite using the Dry Chlorine Extraction Method. Elemental sulphur was produced by Sydney and Frank[16] from pyrite. The general procedure consists of an aqueous slurry, in acid sulphate of suitable pulverized sulphides (100 mesh), in a reaction vessel, at an optimum partial pressure of 100 Ibs/sq. inch and at reaction times of ½ – 2 hours, at 120 – 140°. The reaction yields 67 – 88% S of high purity. Conversion of pyrite to H_2S and S under the action of steam – burning gas mixtures was developed by Noarov and others[17] The pyrite obtained as waste from coal beneficiation contained 35 – 40% sulphur. The resulting gas after the reaction contained 3% H_2S with no S, the residue contained 0.5 – 3% S.

Sulphur and pyrite are plant nutrient. Vera[18] used pyrite earth as fertilizer in Spain. Engrlas[19] found the use of burnt and weathered pyrite as a fertilizer for cereals, vines and trees on meadow lands. It is also used as insecticide and as a preserver of manure. Berillon[20] found its use in vineyards. Vermorel and Dantory[21] showed the increase in yield of wheat and kidney beans upto 30 – 36% by using a mixture of pyrite and dried blood. Kaluzhskii[22] found that the pyrite in presence of phosphorites improves the crops to the same extent as KH_2PO_4, $CaHPO_4$ or Thomas slag. Pyrite residue from coke manufacturing plants can be utilized[23] for fertilization purposes. This is done by oxidizing the pyrite (100 Kg) in the presence of $CaCO_3$ (170 Kg) which neutralizes the free acid formed. About 10% of the pyrite-$CaCO_3$ is recommended for addition to regular fertilizer. Pyrite is also used as a fire retardant. Two fire retardants for wooden roofs were prepared[24] from the mixtures of superphosphate 800, pyrite cinders 320 or 70 and clay 280 or 140 gm/sq.m. Pyrite and superphosphate form Fe-phosphate.

Pyrite has been utilised in cement industry as a raw material. Alekshandrov[25] prepared sulphates and sulphides resistant cement in the usual way from a mixture of limestone, clay and pyrite cinders; the latter being obtained from the sulphuric acid manufacturing plant, Watanabe and Kajii[26] formulated a formula for Cement using pyrite cinder, limestone and clay. Tikhonov et al.[27] prepared a bounding cement consisting of finely powdered mixture of calcium oxide 20%, pyrite 30% and powdered brick 50% having corrosion resistance to salts solutions higher than that of portland cement. Ferrous clay cement[28] was obtained by mixing 20%, lime, 10-30% pyrite cinders and 50-70% fire clay. This cement proved to be stronger and more salts resistant than normal portland cement. Gladysher and Tikhonov[29] made a ferroslag cement containing 15% CaO, 15% roasted pyrites and 70% blast furnace slag. It has comprehensive strength of 392 Kg/sq. cm. after being autoclaved at 8 atm. pressure during hardening. Samples without pyrite treated similarly, has a comprehensive strength of 56 Kg/sq. cm. An Iron-Schist cement, which does not require calcination at 800°, can be prepared[30] by using slaked lime 25, pyrite cinders 15 and schist 60%. Ferrous clay cement[31] was made from a ball mill ground mixture of quicklime 20, burnt clay 65 and pyrite cinders 15% and hardened under different conditions. It showed that addition of $CaCl_2$ and NH_4Cl accelerated the formation of hydrated Ca-silicate and aluminoferrite and ferrite hydrogenated which increased the cement strength significantly; addition of $K_2Cr_2O_7$, NaCl and $CaSO_4$ caused no change; K_2CO_3 and Na_2CO_3 lowered the strength especially at increased temperature. Low alkali and low-aluminate containing cement was produced by Tandilova and his coworkers[32] from a mixture containing limestone 85-88, pyrite cinder 1-2 and alunite mud as clay component 11-13 Wt.%.

Binders and special materials for different purposes were prepared form pyrite and different chemicals. A noncalcined binder, obtained by grinding and mixing of slaked lime 20, pyrite cinder 30 and burnt clay 50% has highest strength[33] Samida[34] prepared a binding agent and a filler from a homogeneous mixture of butadiene-styrene rubber 12, bakelite cement 12, ground sulphur 1.5, MgO 1.0, asbestos 53.5 and calcined pyrite 20 Wt.%; it was

advised to press the product at 140 – 160°, 200 – 300 Kg/cm^2. for 1 min/mm of lining thickness. A new binding material of the silicate hydrogarnet type was obtained[30] by grinding slaked lime 20, pyrite cinders 5 – 10, clay (glinite) 70-75% until 10 – 15% passes through sieve No. 0085. Asaulyake et al[35] prepared a binder from phenolic resin and polystyrenegranules using Al-Cr-phosphate and various mineral fillers including pyritic ore. A 62% content of mineral fillers decreased the phenolic resin consumption 20-30%. Material resistant to abrasion at high temperature and useful for the preparation of brake, clutch linings, grinding wheels and generator brushes etc. were prepared from 5 – 95% prepolymer, obtained by heating 1.3 – 5 moles of (p-$C_4H_2O_2N - C_6H_4$) – CH_2 with one mole of (p-$H_2N\ C_6H_4)_2$ and 5 – 95% thermostable fillers e.g. corundum, Fe-pyrite, lithopone, graphite, asbestos fibers or Mo-sulphide. The mixture was pressed one hour at 250° and 200 bars into 70 x 12 x 5 mm sticks having 800 Kg/cm^2 binding strength at 25° and 450 Kg/cm^2 after heating 100 hours at 250°[36]. Bundnivkov et al[37] introduced raw material mixture for the light weight filler, contained a highly expanding clay 97 – 98% and an additive of a powdered pyrite cinders 2-3%. The additive was used to decrease the bulk density of the product. Refractory mortar for the lining of rotary kilns was prepared by Matveeva and Napsikov[38] suing the ratio wt. of magnesite powder with $\leqslant$ 0.6 mm grains 50-60, water glass 70-75, pyrite cinders 20-25 and technol dust collected from cement kiln waste gases 20-25 parts by wt. Polymer concrete were prepared from monomor FA 7-9, $C_6H_5SO_3H$ 2 – 2.5, granitic coarse aggregates (pyrite of fluorite) 54-55, quartz sand 24-26 and other fine aggregates 9 – 11 wt.%[39]. The aggresive action of water on polymer concrete is accompanied by (I) softening of bond due to swelling of polymer (II) dissolution of binder components in water and (III) chemical action of water on polymer. The water resistance of polymer concrete is increased by using aggregates of pyrite, fluorite, hornblend and graphite and by treating quartzose aggregates with organo-silicon, epoxy resin and furan ligomers. Heinrich and Weisel[40] formulated a polymeric composition for coating articles, metal surfaces fabrics, felt, carpet backing etc. A polyamide fiber tuffed polyester felt carpet was back coated with a composition containing emusion PVC 100 dioctyl phthalate 110, roasted pyrite 200, alkyl benzene 5 and Ba-Cd-liq. stablizer 1.5 parts wt. to give 2.8 Kg/m^2 and gelled at 174°, giving a coating with surface resistance 1.0 x 10^9 Ω cm. and sp. vol. resistance 4 x 10^9 Ω cm.

The material used for the manufacture of Amber glass[41] contained sand 907.2, soda 318.1, limestone 172.4, slag 120.6, Fe-pyrite 2.28, gypsum 6.10 and ferric oxide 1.20 Kg, where-by the slag contained SiO_2 38.90, Al_2O_3 + TiO_2 9.75, CaO, 40.60, MgO 8.20, Fe_2O_3 0.25, MnO 0.50, Na_2O + K_2O 0.70, SO_3 0.14 and S 0.75% which was used as colouring agent to introduce the stoichiometric sulphur for the FeS formation. Magnetic glass[42] was prepared by heating a mixture of 1 – 5 alkali metal aluminosilicate mineral and 1 wt. part Fe-sulphide mineral to form an amorphous magnetic fraction which was heated in a limited air atmosphere at 1200 - 1600°, thus 5 sericite ore was ground to 70 mesh with 1 wt. part pyrite and melted at 1250° overnight and slowly cooled from 1200-200° in 4 hours. The room temperature products was a black, amorphous magnetic material.

Pyrite and marcasite are used as indicator electrodes in oxidation-reduction titrations. A pyrite-Pt pair gives a differential titration curve. In alkali solution pyrite, marcasite and platinum responds almost identically to changes in the concentration of sulphide, the single electrode potentials being shifted 120 mv. neg. for each 10 fold increase in sulphide concentration[43] After wards Markorov and coworkers[44] developed the similar type of pyrite indicator electrode for neutralization reactions during potentiometric titration owing to the formation of an electrochemical system between Fe (II) and Fe (III) ions and sulphide electrode.

For the manufacturing of Pellets[45] in the Kowa process, pyrite is roasted in a fluosolids roaster and the SO_2 gas is utilized for manufacturing H_2SO_4, some $CaCl_2$ is added to the cinders and the mixture is converted into balls 10-15 mm. in diameter, which are dried and then heated in a rotary kiln to $\leqslant$ 1250° in an oxidizing atmosphere. In the Kiln non-ferrous metals, such as Cu, volatilized as chlorides and the $CuSO_4$ decomposed; the cinder emerge as strong burnt desulphurized pellets. The gas produced is treated by a wet system to recover valuable components . The refined pellets have a crushing strength of $>$ 300 Kg. and good charge material for blast furnance. The features of this process are purification

and pelletizing which are carried out simultaneously, the degree of removal of Cu, Zn, etc, is higher than in conventional chlorination roasting and leaching process and the recovery of Au, Ag and Pb is better. Self-fluxed pellets of low metal impurities[46] were prepared by mixing pyrite cinders containing Fe, 56.26, CuO 4.13 and ZnO 3.66% and ground with 3.5% $CaCl_2$ and 2% gypsum; the mixture pelletized to 10 – 13 mm., dried at > 200° and roasted at 1200° to volatilize Cu, Zn and S. Paul[47] performed experiments for the production of low cost acid-ferric-sulphate solution for chemical mining from pyrite.

Chekurov et al[48] prepared a solid medium for sulphocyanocoating, contains yellow potassium ferro cyanide 20-40 and pyrite 5-15% and the remainder chamotle. Desulphurization of petroleum containing S 3% was carried out (49) by contacting pyrite cinders and then autoclaved at 380°; the desulphurization was 71% after 1.1 hours treatment. Robota[50] developed a process for halogenation of aromatic hydrocarbons; PhMe or PhCl were ring-chlorinated by gaseous Cl in the presence of a catalyst FeS or pyrite. Alkyl bromide were prepared (51) by the treatment of alcohols with Br in the presence of pyrite at elevated temperature; the conversion was higher in the presence of H_2O and Cr or Mn-oxide. Baccaredda[52] manufactured CS_2 from different types of pyrite and CH_4 at 600-750°. Vornousku et al[53] prepared polymeric materials from PVC, di-Bu-phthalate and Ca-stearate containing upto 70% fine pyrite residue, the tensile strength of plates reaches a maximum value at 35% of pyrite and the elongation at break decreases and hardness increases with increasing concentration of later one.

The residue left after roasting pyrite is called cinder and can be used as raw material for iron industry after desulphurization. Guedras[54] described a process for the manufacture of cast iron from pyritic cinders obtained from sulphuric acid plant, containing 94% Fe_2O_3, 3% SiO_2 and 2.75 – 3.5% S. The process consists of complete dehydration, desulphuraization by Calcium choride, agglomeration in a horizantal rotating furnace at 1000-1200° and reduction with coke, charcoal or anthracite and charcoal in a Siemens type electric furnace.

Ongaro[55] desulphurised the pyritic cinders in an electric furnance by a chlorinating process using soda ash, Carbon, Calcium oxide, magnesium chloride, magnesium oxide as fluxes. Ficai[56] commercially utilized pyrite ashes as an iron ore. Stanley (57) heated pyrite in the absence of air to about 700-900° and the solid monosulphide residue was treated with strong HCl at an elevated temperature to form a solution containing ferrous chloride which crystallized and then heated in air and moisture to form HCl and Fe_2O_3. Achille[58] obtained pure iron oxide by reducing pyrite with hydrogen at 460-600° to give hydrogen sulphide and iron monosulphide with 20% HCl. The ferrous chloride solution was evaporated and then treated with steam at 500-600° to obtain pure Fe_2O_3 and HCl. Lesokhin[59] described the process for the production of iron powder from pyritic cinders, obtained as a by-product from sulphuric acid plant. Damskaya et al[60] directly produced sponge iron from pyritic cinders in fluidized bed furnace. Eketrop[61] obtained pure iron oxide from pyrite by using Flotation Method, with better control of the roasting operation and used it as a raw material in iron and steel manufacturing. Pyrite cinder has been utilised in iron oxide pigment industry. Kiriyama and coworkers[62] manufactured sulphur-free-cutting steel. In an oxygen upflow rotary furnance, a mineral of Fe-sulphides (5.1 Kg/ton) containing S 45.3, Fe 44.2, SiO_2 3.0 and Al_2O_3 0.14% was added to molten pig iron at 1650° and the basicity was adjusted to 2.5. The resulting sulphur-free-cutting steel contained 0.17% S as compared to 0.03 - 0.04% S with the addition of Fe-sulphide mineral in convention methods.

Shifrin[63] produced sulphuric acid by the oxidation of the mixture of pyrite flotation tailings and slag, obtained at the end of the process with nitric acid. Hook[64] used spanish pyrites for the manufacture of sulphuric acid by Lead Chamber process. Yazaki[65] described a procedure for the manufacture of sulphuric acid by the utilization of gas from atmospheric nitrogen fixation. Pyrite of poor quality (32% S) was heated for an hour apporximately at 800° with nitrogen containing gases fixed from the atmosphere to change all the sulph ır to sulphur trioxide and iron to ferric oxide. A simple method for preparing sulphuric acid was described by Junginer[66] involving the combustion of pyrite in the presence of nitrogen, oxygen and sulphur dioxide; separation of the sulphur dioxide by silica gel adsorption and followed by catalytic oxidation to sulphur trioxide (90% conversion); which was then

absorbed by 98% sulphuric acid. recycled sulphur dioxide and the subsequent step could be recyeled in the combustion furnace. Sodium sulphite was prepared by adding an equal amount of sodium carbonate to the saturated solution of sulphur dioxide obtained from roasted pyrite and evaporating the liquid for crystallization.

Many inorganic metallic compounds were prepared from pyrite on commercial scale. The ores especially copper containing pyrite and chalcopyrites containing 8 - 10% Cu were concentrated by flotation, agglomerated, roasted at $< 700^{o}$, hydrated, ground with small amounts of lime, diluted during recycled, neutralized and filtered[67] The filterate was allowed to crystallize to form $CuSO_4$ cake, which was washed with acid. From these washings Cu $(OH)_2$ was precipitated and recycled. Removal of copper was performed by roasting the pyrite cinders in air containing atleast 1% chlorine at 700-1000^{o} for atleast one hour, resulted 90% removal of copper (68,69). Copper was effectively and economically extracted as $CuCl_2$ from pyrite cinders by conversion of sulphide into oxides at 1100-1300^{o} and immediate chlorination at 1000^{o} with Cl_2[70] . Thus Cu content in pyrite cinder pellets containing Fe 60.0, Cu 0.6 and S 1.00 was reduced to 0.047% and the exhaust gas from the chlorinating furnace contained $\sim$ 0.046 gm. Cu/L.

Ferric hydroxide was prepared by Timkin[71] by dissolving pyrite cinders in HCl and the resulting solution was treated with NH_3 at pH $\leqslant$ 4. The precipitated Fe $(OH)_3$ was treated by known procedure, the mother liquor is regenerated by lime suspension and thus obtained NH_3 was returned into cycle. For the preparation of ferrous chloride, pyrite was roasted in an electric furnace at 900-940^{o} in the presence of natural gas (Cn H_2n 37.0, CH_4 46.3, H_2 12.4, CO 4.0 & 0, 0.3%) and steam. The percentage of sulphur was reduced from 5.8 to 0.04% and Fe as FeO was dissolved in 1NHCl. After filteration $FeCl_2 \cdot 2H_2O$ was obtained in chemical pure grade with one recrystallization[72] For the concentration of iron, the pyrite cinders were reduced at 300-600^{o} for few hours with CO, and equal mixture of CO and CO_2 and with CO, CO_2 & N_2 (1 : 2 : 10) consequently, the reduced cinders were exposed in a magnetic separator to a field of 40 or 80 gausses and thus Fe obtained was found to be 50 to 60%[69]. The process of formulation of Mn-ferrite in roasting of mixture of MnO_2 and pyrite in air was investigated by means of thermobalance, differential thermal and X-ray analysis. The production of $MnSO_4$ from roasted MnO_2, starts at $\sim$ 400^{o} and this product decomposes to Mn_2O_3 or Mn_3O_4 at 700-900^{o}[73] Fe_2O_3 was produced by roasting the pyrite at $> 700^{o}$ and at $> 900^{o}$. Mn-ferrate was formed by the reaction between Mn_3O_4 and Fe_2O_3.

Pitchblend ore was prepared for leaching with water by mixing with about 10% pyrite by Wt. and passing the 60 mesh mixture slowly through a multiple hearth[74] On the upper hearth, temperature of the charge was slowly raised from 167-480^{o} to decompose FeS_2 and to produce SO_2 and Fe_2O_3. On the middle hearth, the temperature was increased gradually to 600^{o}; SO_2+O_2 was catalysed by Fe_2O_3 to SO_3. On the lower hearth at about 600^{o} these reactions were completed and other sulphates such as $Fe_2(SO_4)_3$ were decomposed into insoluble oxides so that only U-sulphate was dissolved in the subsequent leaching. Each of the three stages required 4-8 hours. Susarov[75] showed that the powder from pyrite works was washed with water, ground and heated to 600-900^{o} for 3 hours, it was then used for Fe_2O_3 pigments. Khan and Yousuf[7] desulphurized the pyrite by fusing with Na_2CO_3 and then roasting at 900^{o}, produced SO_2 and Fe_2O_3. The later one was of pigment quality.

Commercial preparations of Na_2S and Na_2SO_4 from Hyderabad Iron Pyrite are described by Datar et al[76]. A fusion of iron pyrite with Na_2CO_3 and half its weight of coal for 3 hours at 900^{o} followed by water extraction produces Na_2S in solution. As an alternative method, iron pyrite is heated in air with Na_2CO_3. Na_2SO_4 is obtained by water leaching. $BaSO_4$ is reduced to BaS by heating it with 0.5 its weight of coal at 800^{o} for 6 hours. The residue is heated with Na_2SO_4 solution thus Na_2S is produced and $BaSO_4$ is regenerated for re-use. Pyrite catalyses chloriantion of both Fe and Ti unselectively[77].

Conclusion

It is observed by many workers that the particle size of pyrite ore is an important factor for the complete reaction. In general 80 mesh ore is used for industrial exploitation but on experimental basis 100

mesh gives better results[7] . If any pyrite ore contains even small percentage of nickel or copper that deposit is economcally profitable and iron and sulphur are obtained as a by-product because copper and nickel are much more precious metals than iron and sulphur. Such deposits besides their small reserves, for flung locations and very short working period can be exploited economically. The absence of arsenic is very remarkable because its presence in the ore poses a great difficulty in the production of sulphuric acid. It poisons the catalytic property of platinum, which is used as a catalyst in the Contact process. It is therefore, additional units such as dust chamber and scrubber are to be employed in the sulphuric acid manufacturing plant to remove the arsenic oxide from exhalant gases containing sulphur dioxide before these are fed to the catalyser portion of the plant. The presence of vandium in a pyrite is a great assest to oxidation process, as it can be used as catalyst in place of very costly platinum metal, oxidizes sulphur dioxide into sulphur trioxide.

The Reshian pyrite is the only deposit is Pakistan which contains higher percentage of iron and sulphur as compared to other pyrites[5]. Preliminary exploration[6, 7] showed that the reserve is sufficiently large. But further extensive exploration of the deposit and the survey of the adjoining areas has not yet been carried out to prove the additional reserves. The presence of vanadium metal may be expected in association with pyrite in the additional reserves, as it is often present in good pyrites and thus increases the commercial value of the deposit, as this deposit is situated in farflung high altitude areas and the problem of transportation and short working period due to winter snow may lead the establishment for a mining unit tc uncommercial. But its chemical analysis showed[7] large percentage of iron and sulphur (Samples from main pyrite body, Fe 45.24 & S 53.35; samples from vein Fe 32.33 & S 34.77%) and both these components can be separated by improving and enlarging the methods as mentioned in previous pages. The iron oxide as a raw material will fulfill the required standard of an iron ore for iron and steel industry and the exhalant gas can be used for the preparation of sulphur compounds and in the preparation of wood pulp which is extensivley used for the manufacturing of paper[12]. Actually, the exhalant gases mainly sulphur dioxide is insignificant as a by-product but if elemental sulphur is precipitated out of the gas, it may prove appreciably economical.

REFERENCES

1. R.N. Ghosh, *Geol. Soc. India Bull.*, 4 (3), 77 (1967).
2. H.J. Ward, *Econ. Geol.*, 56, 402 (1961).
3. Ch. D. Dzhafarov, *Rentgenogr Mineral Syrya Akad. Nauk SSSR*, 3, 35 (1963).
4. A. Zaki, *Directory of Mineral Deposits of Pakistan*, 15, (3), 200 (1969).
5. A.M. Heron, *W.P.I.D.C. Mineral Deposit Report*, (II), 23 (1968).
6. S.H. Farooqi, *Rept. on Pyrite Deposits in Reshian Azad Kashmir*, 6 (1969).
7. A.K. Irshad, M. Yousuf, *Sci. and Indi.*, 9, 3, & 4, 198 (1972).
8. S.K.L. Rao, *Indian Miner.*, 25 (4), 340 (1971).
9. A.K. Ghosh, *Geol. Soc. India Bull.*, 5 (1), 16 (1968).
10. S. Robson, *Trans. Inst. Chem. Eng. London*, 43 (1954).
11. L. Dorenfeldt, *J. Wochbl. Papierfabr*, 4, 614 (1909).
12. H. Freeman, *Pulp Paper Mfg. Can.*, 32 167 (1932).
13. K.M. Malin, *Vaprosy Poluchem. Sernist. Gaza. Kolchedanaisery*, 101 (1957).
14. W.A. Hall, *U.S.A. Patent*, 1, 133, 636, March 30 (1914).
15. R.C. Rowe, *Can. Minig J.*, 59, 181 (1938).
16. N. Sydney and A.F. Frank, *Sherritt Gordan Mines Ltd. Can.*, 683, 663, April 7 (1964).
17. I.A. Noarov, V.M. Ivanov, P.N. Galushko, O.P. Kirsanova and E.I. Shmuk, *Khin. Tverd. Topl. (Russ)*, 3, 87 (1971).
18. V. Vera, *Prog. Agr. Y. Pecuario*, 16, 684, 419, 686, 452 (1910).
19. F.H. Engrals, *Engrais*, 25, 1028 (1910).
20. Berillon-Moreau, *Engrais*, 26, 378 (1910).
21. V. Vermorel and E. Dantony, *Engrais*, 28, 1304 (1913).
22. A.A. Kaluzhskii, *J. Applied Chem. (USSR)*, 5, 117 (1932).
23. Felicissimo Jesuino, Jr. *Mineracao Met.*, 51 (301), 3 (1970).
24. V.Ya. Livshits, *Byull. Tekh. Inform. Stroitel. Leningrad. Glann. Stroitel. Upravlenpri, Leningrad. Gloan. Stroitel. Upravlenpri, Leningrad. Gorod. Ispolnitel. Komitate, 44, 16 (1958).*
25. I.A. Alekshandrov, *Neftyanoc Khazyaistov*, 17, 193 (1929).

26. K. Watanabe and M. Kajii, *Ube Industries Ltd. Japan,* 57, July 12, 4865 (1957).
27. V.A. Tikhonov, L.G. Shpynova and E.V. Zdauevich, *Polytech. Inst. Lvov.,* 418 (1958).
28. V.A. Tikhonov and E. Zukhovitskii, *Polytech. Inst. Ivov.,* 2, 209 (1959).
29. B.M. Gladyshev and V.T. Tikhonov, *Stroitel Materialy,* 7(2), 30 (1961).
30. V.A. Tikhonov, *Ukr. Khim. Zh.,* 32(10), 1127 (1966).
31. M.I. Lisetskii, *U.S.S.R. Zb. Nauk. Rob. Aspir. Lviv. Politekh. Inst.,* 6, 122 (1972).
32. K.B. Tandilova, Ya.K. Grineriya, O.S. Dzhadzhanashvili, T.G. Gabadaze., *U.S.S.R. 381, 625 (Cl. Co4b),* May 22 (1973).
33. V.A. Tikhonov, L.G. Shpynova, E.V. Zdanevich and E.M. Polyanskaya, *Dokl. Lvovsk. Politekhn. inst.,* 2 (2) 139 (1958).
34. Z. Smida, *Czech. 119, 636 (Cl. B29b),* Aug. 15 (1966).
35. E.M. Asaulyak, B.P. Gusev, I.F. Ustinova and L.I. Shullgina., *(U.S.S.R) Tekhnol. Sovistva Fostatnykh Mater (RUSS),* 115 (1974).
36. Laurent Serge, mallet Maurice, *Ger. Offen. 2000, 855. (Cl. C08f),* 3 Dec. 1970, Fr. April 10, Jan. 26 (1969).
37. P.P. Budnikov, V.I. Zharkovskii, R.M. Froze, N.D. Zolotnitskii and N.S. Shustrova, *USSR 299, 490 (Cl. C04b),* March 26 (1971).
38. R.D. Matveeva, V.A. Napsikov and O.I. Soloveva, *USSR 307.077 (Cl. C04b),* June 21 (1971).
39. V.I. Solomatov, *Beton Zhelezobeton (RUSS),* 8, 21 (1974).
40. D. Heinrich, G. Weisel, *Ger. Offen. 2, 438, 560, (Cl B05D),* 26 Feb. (1976), Appl. 2438, 5602, 13, Aug. 10 (1974).
41. C. Calumite., *Ger. Offen. 2 326, 833 (Cl. C03C),* Dec. 6 (1973).
42. E. Lee Thomas and M. Laurent Sebastian., *U.S. 3,900, 415 (Cl. 252 62.51, CO4b, HO1f, CO3C),* Aug. 19 (1975).
43. Pringle, L. David, *Diehl. Harvey Proc. Iowa. Acad. Sci.,* 72, 161 (1967).
44. G.V. Makarov E.A. Buketov M.A. Edrisova and L.G. Kozorin *Zh. Anal. Khim (RUSS),* 29 (4), 801 (1974).
45. Yasutake Okubo *J. Metals,* 20 (3), 63 (1968).
46. Y. Ohkubo and Ogasawara Masaki, *Kitazawa Tadao Japan 7403, 606 (Cl. C21b C22b),* Jan. 28 (1974).
47. H.J. Paul., *Nevada Bur. Mines. Rept.,* 13 (B), 75 (1966).
48. V.V. Chekurov, A.A. Mukhamedov and O.B. Romanov, *State Design Construction Technological Bureau of Machine Building, USSR, 254.995 (Cl C23C),* Oct. 17 (1969).
49. N. Negishi and T. Sakai, *Japan 73, 11, 321 (Cl. C10g),* Apr. 12 (1973).
50. S. Robota, R. Paolieri and J.G. Mc. Hugh, *Ger. Offen. 2447,932, (Cl. C07C),* Apr. 24 (1975).
51. O.V. Lebedev and L.D. Zelenina, *USSR 475, 353 (Cl. C07C),* June 30 (1975).
52. M. Baccaredda, G. Nencetti and G. Giglioni, *(Univ. Pisa. Italy) Chim. Ind. (Milan),* 45 (7), 777 (1963).
53. N.E. Voronovskii and V.A. Voskresenskii, *Izv. Vysshikh Uchebn. Zavedenii. Stroiti. Arkhitekt. (RUSS),* 8 (8), 76 (1965).
54. M. Guedras, *Tech. Moderne,* 12, 1301 (1920).
55. G. Ongaro, *Griorn Chim. Ind. Applicata,* 3, 288 (1921).
56. C. Ficai, *Griorn. Chim. Ind. Applicata,* 9, 450 (1928).
57. I.L. Stanley, *U.S. Patent, I. 980, 809,* Nov. 13 (1934).
58. P. Achille *Ital. Patent, 541.555,* Feb. 10 (1955).
59. I.G. Lesokhin, *Trudy Leningrad, Tekhnol. Inst. Im. Lensoveta,* 54, 82 (1959).
60. G.I. Damskaya, S.S. Tikhonov and G.Y. Leizerovich, *Tsvetnye Metally,* 33 (4) 29 (1960).
61. S. Eketrop, *Jernkontorets Ann. (Swed.),* (5), 148 (1964).
62. S. Kiriyama, T. Hirayama, T. Dane and T. Fujii, *Japan 7031, 052 (Cl. 10J14)* Oct. 7 (1970).
63. M.V. Shifrin, *J.Chem. Ind. (USSR),* 2, 18 (1940).
64. W. Hook, *Gas world,* 136, 3555, 57 (1952).
65. T. Yazaki and K. Nakajima, *Bureau of Industrial Technics Japan,* 51, 5971 Oct. 8 (1952).
66. A. Junginer, *Molecalini Societa Generale Per. 1. Industria. Minnerariae Chemica (Ital.),* 688, 338 March 29 (1965).
67. F.E. Nasturzio, *Miniera di Libiola Societa in Accomandita Semplice Ital.,* 560, 855 Apr. 12 (1957).
68. K. Okajima, M. Inouye and K. Sano, *Mem. Fac. Eng. Nagoya Univ.,* 11, 160 (1959).
69. K. Hirose and I. Yano, *Ryusan,* 12, 56 (1959).
70. K. Meyer and H. Pietsel, *Metallgesell-shaft Ger. 1, 133, 560 (Cl. 40a),* July 19 (1962).
71. N.I. Timkin, *USSR 123, 524,* Nov. 9 (1959).
72. V.G. Nikitina, *Trudy Gorkovsk. Politekh. Inst.,* 15 (5), 76 (1959).
73. S. Sakairi, *Iwate Daigaku Kogakubu Kenkyu Hokoku Japan* 17, 1 (1964).

74. A. Oscar. Fischer, *U.S. 3, 152, 862 (Cl. 23-14.5)*, Oct. 13 (1964).
75. M. Susarov, *J. Chem. Ind. (USSR)*, **15** (12), 43 (1938).
76. D.S. Datar, K.N. Moorthy and Razia Usmani, *J. Indian Chem. Soc. Ind. and News Ed.*, **14**, 28 (1951).
77. R. Manocha, *Trans. Indian Inst. Metals*, 7, 104 (1955).