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Silica based Product Identified for Production from Kimberlite Tailing

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Abstract

National Mineral Development Corporation is involved in diamond mining in the country & Kimberlite produce as a mines waste during kimberlite mining .N M D C is producing around 0.9 million tones of Kimberlite per year in Panna.. With estimated life of 20 years for Panna mines , it is pertinent to look for commercial application of kimberlite . Around 3-4 million tones of Kimberlite is already available from Panna mines accumulated during previous mining . Due to the fact that Kimberlite / Diamond ratio is 100 tones of kimberlite per 10 carat of Diamond produced, there is a need to look for development of multi – product which are of bulk usage from the Kimberlite. Technological option for Eco- friendly & Economically Efficient Utilization of Kimberlite needed and in view of their wide application, also bulk usage, the following three products were identified to be developed from Kimberlite.

Sodium Silicate	*Sodium Silicate because of their exceptional properties and their relatively low cost has widespread usage in many industries. It is used in manufacture of Soaps and Detergents which contain around 5 - 15% Sodium Silicate.*
Precipitated Silica	*The oldest and most important use of Precipitated Silica is the reinforcement of elastomer products such as Shoe soles, technical rubber article and cable sheeting and tire components.*
Zeolite–A	*Zeolite – A has replaced the Phosphate in household detergents, it act as water softener due to its ion exchange behavior.*

The technology has been demonstrated through pilot scale operation, process has been established and filed for patenting. There is no reference on the synthesis of these products from Kimberlite in open or classified literature. Therefore, this is a novel and challenging application of Kimberlite. The phenomenon poses a double pressure on the diamond industry, to lower cost and to keep growing. This call for focus on large scale, long life, cost conscious industrial operation having Ecofriendly and safe performance.

INTRODUCTION

Kimberlite

Kimberlite is a basic rock produced by the volcanic activity from great depth within the earth. Kimberlite occurs in "Kimberlite Pipes", vertical columns of rock that rise from deep magma reservoirs (1).

In the earth's crust, graphite is the thermodynamically form of carbon. Diamond is stable only at high pressure as found in the zone of the earth's mantel. As a natural mineral, diamond is found in kimberlite which is basic rock produced by volcanic activity. Chemical composition (Wt.%) of raw kimberlite were shown in Table 1. From the table, it is inferred that the Silica and Magnesium are the major constituents in the Kimberlite.

Table 1: Typical Chemical Composition (Wt %) of Raw Kimberlite

Constituents	Assay %
SiO_2	30 - 32
Al_2O_3	2 - 5
TiO_2	5 - 8
CaO	8 - 10
MgO	20 - 24
Fe_2O_3	5 - 11
LOI	13 - 15

As the Kimberlite rocks are rich in magnesia and silica, efforts were made to prepare value added product like Sodium Silicate, Precipitated Silica and Zeolite –A.

Sodium Silicate

Sodium Silicate are generally water soluble silicates. Basically they are constituted by three compounds (a) M2O, (b) SiO2 (c) H2O. General formula of silicate is M2O.SiO2.H2O, where M can be any one from Na, K, or Li.Generally, three types of commercial silicate are available in market differentiated by their SiO2/Na2O mole ratio and specific gravity. (1) Sodium Meta Silicate – Silicate having SiO2/Na2O mole ratio 1.0 which can be obtained by direct fusion method, it is high alkalinity.(2) Sodium Ortho Silicate – silicate having SiO2/Na2O mole ratio< 1.0, produced by blending anhydrous sodium silicate (ASM) and NaOH.,(3) Neutral Sodium Silicate - silicate having SiO2/Na2O mole ratio> 3.0 (2).

Precipitated Silica

The term precipitated silica evidently indicate and falls in to function form of the precipitated type(3)They are prepared by destabilization of sodium silicate molecule under condition that avoid the formation of continuous gel structure .Synthesis of silicon is done by neutralization of sodium silicate at elevated temperature. First the dilute sodium silicate is heated up to the reaction temperature and it is neutralized by acid under controlled reaction condition in presence of electrolyte. When sodium silicate solution is neutralized with an acid so that colloidal particle will grow in weakly alkaline solution and be flocculated by the sodium ion of the resulting soluble sodium salt to precipitated silica(4).

Zeolite- A

Zeolite is crystalline Alumna silicate with regular three-dimensional porous lattice structure built up from $SiO4^-$ and $AlO4^-$ tetrahedral in which the negative charges are compensated by mono or multivalent cat ions. These cations are exchangeable without lattice structure being destroyed. This property explain the reason for their use as water softener in house hold detergents substituting sodium tripolyphosphate (STPP). Due to the increasing polluting effect of phosphate and their non – biodegradable property , it is not advisable to use STPP in detergent powder. Under these circumstances use of Zeolite-A is increasing day by day as detergent builders (5,7).

RESULT AND DISCUSSION

Sodium Silicate

The Silica rich kimberlite was used as a raw material for preparation of sodium silicate. Wet chemical analysis was done for characterization of sodium silicate. The physico-chemical properties of sodium

silicate are given in Table 2. From the table it is inferred that the sodium silicate is a neutral sodium silicate and it can be use for preparation of precipitated silica and zeolite-A. Specific gravity Vs SiO2 concentration is given in Fig.1 which will help to know the unknown concentration from sp. gr.of solution However maximum silica content is 18-19% above that silica starts to polymerize. Commercially available, chemical grade sodium silicate having SiO2:Na2O mole ratio equal to around 3 can be prepared in this process, which is generally used in the process for manufacturing of precipitated silica and zeolite A. Production and Applications of Sodium Silicate:-

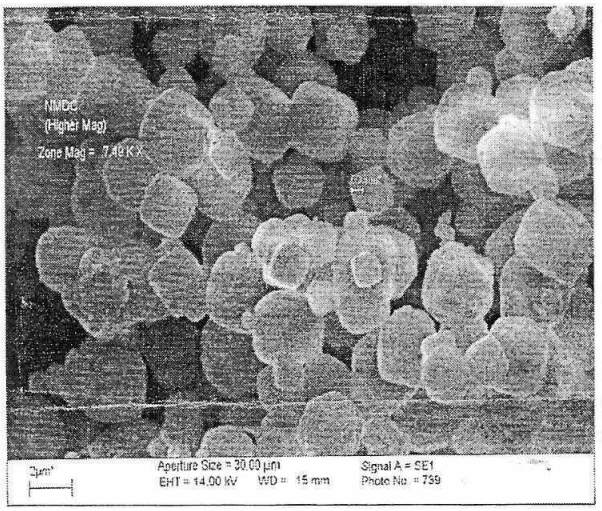

Fig. 1

Table 2: Physico –Chemical Properties of Sodium Silicate

Properties	Value
SiO2	12-14 %
Na2O	3-4 %
Sp.gr.	1-1.2 %
Insoluble matter	Max.0.5%
Mole ratio	Around 3.

Around 4 million tonnes of soluble silicates are produced annually all over the world. Nearly 30% are used by the detergent industries, 37% by pigment, catalyst and gels. The balances find use in adhesives, cement, building materials and other uses.

Derivatives:	
Zeolites/Alumino Silicates	36%
Precipitated Silica	18%
Silica gel	4%
Colloidal silica & others	3%
Direct Uses	
Soaps, detergents and cleaners	19%
Pulp and paper	9%
Adhesives, cements and coatings	6%

About 5 lakh tonnes per year (on 100% basis) of total soluble silicates are produced by more than 400 small-scale industries in India. Soluble silicate industry in India has a stunted growth because the industry is reserved for small-scale sectors. The economic viable plant capacity of soluble silicate internationally is a minimum of 1000 tpd capacity.

Precipitated Silica

The raw material Sodium Silicate were used for preparation of precipitated silica, the physico-chemical properties of Precipitated Silica were given in Table 3.From the table it is inferred that the Precipitated Silica is very good quality of silica where in only 1 % is the insoluble salt, particles size are also suitable for rubber industries.

Table 3: Physico-Chemical Properties of Precipitated Silica

Properties	Value
1. Appearance	White amorphous powder
2. Bulk density a) Before Taping b) After Taping	 0.09 0.1
3. Oil absorption value	225%
4. Water absorption value	245%
5. PH of 5% aqueous slurry	7.0
6. Moisture at 105 degree C	5`4
7. Loss on Ignition	6`5
8. SiO_2	87`5
9. Particle size (-325BS mesh)	99%
10.Soluble salt	1.0%

Precipitated silica were used as reinforcing agent in silicone rubber. In thermoplastic, precipitated silica were used to improve specific properties. They act as antiblocking agent and are to prevent plate-out effect in film and film production. They are also used to improve the mechanical properties of PVC flooring. A further major application is, use as carrier silica's for liquids and semi liquids and free flow agents for powder formulation, particularly of hygroscopic and caking substances.

Production and Application Precipitated Silica in India
Indian Production capacity is around 35,500 tpa with about 50 manufacturers in the country.

Major producers in India:	tpa
Degussa (earlier Insilico), UP	13,000
J.M. Huber, Gujarat	7,000
Madhu silica & Aquagel, Gujarat	7,500
Anandiya	5,000
Others	3,000

Annual Consumption Pattern in India
(15% annual growth rate in nineties and 7-% in recent years)

Tyre	6,000
Footwear	3,000
Other rubber goods	2,500
Cosmetics	5,000
Pesticides/detergent	5,000
Pharmaceuticals	2,000
Paint/adhesives & other specialties	2,000
Export	10,000

Potential Areas

Toothpaste, Condom grade, Polymer grade

Global Production and Application of Precipitated Silica

World Production capacity is estimated to be around 800,000 tpa with Europe, America and Asia corresponding to 340,000, 260,000 and 200,000 tpa respectively. The major producers include: Degussa, Rhone-Poulenc, Akzo and Cross field in Europe and PPG and Huber in the United States. Asian market is additionally supplied by local producers. Typical Consumption Pattern of precipitated silica are shown in Fig2

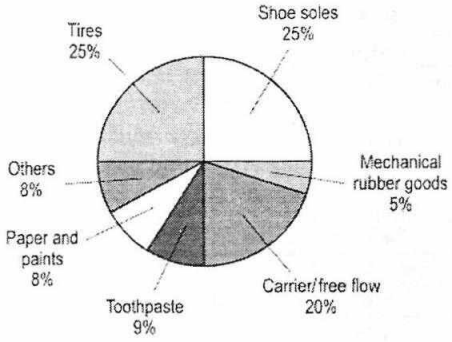

Fig. 2

Table 4: Physico-Chemical Properties of Zeolite-A

Properties	Value
1. Appearance	Fine powder
2. Whiteness index	0.98
3. Calcium Binding capacity, Mg Ca/g	160,minimum
4. Loss on ignition	20.5%
5. PH of 5 %aqueous slurry	11.0
6. Particle size ,um	d(50) 2-4 d(100) 25max
7. Chemical Analysis SiO2 % Al2O3 % Na2O %	 35.55 28.25 15.25
8. Crystalinity	>98
9. Bulk Density	0.4 to 0.6

Zeolite-A

Sodium silicate was used as a raw material for preparation of zeolite A for characterization of zeolite A. XRD, SEM and chemical analysis were taken & specification of sample are given in Table no. 4. The crystalline structure was conformed by powder XRD of the product, which is shown in Fig3.and it is indicate the formation of zeolite-A. The product was also analyzed for particle size distribution by laser diffraction technique using Master sizer 2000. (Malvern Instrument Ltd., UK)

XRD of the zeolite –A sample (oven dried) prepared at NMDC

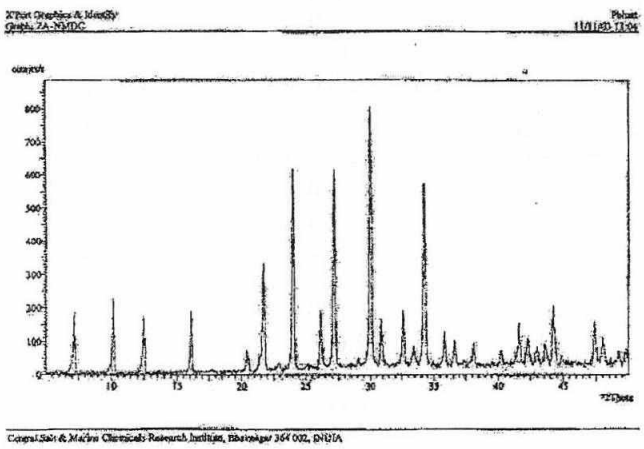

Fig. 3

The properties of Zeolite-A which leads to its use as detergent builder are (6)

- The Zeolite is highly effective in removal of water hardness ions, particularly calcium, both at ambient temperature and higher temperatures.
- It gives alkaline reaction in aqueous medium with PH less than 12.
- It dose not cause encrustation on the fabric.
- Zeolite A crystals are cubic in shape with rounded corners and edges (see in Fig.4) and can pass through the pores of the fabric allowing easy removal during washing.

- The surfactant adoption capacity of the zeolite is several times higher than the polyphosphates.
- The zeolite absorbs unwanted water- soluble molecules from the dirt.
- It coagulates the colloidal dirt particle and pigments causing easy removal from the aqueous phase.
- It does not clog the sewerage.
- It does not exert any negative influence upon biological sewerage purification.
- It does not remobilize heavy metals.
- The zeolite is toxicologically innocuous.

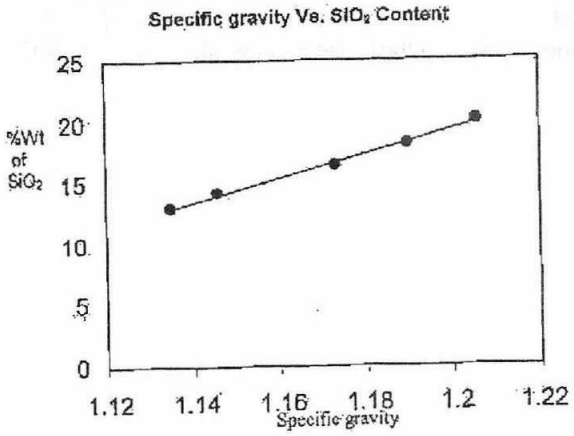

Fig. 4

Production & Applications of detergent grade Zeolite AFor traditional consumer laundry powders, around 25-30% of a detergent formulation are a builder like STPP or zeolite A. The global demand for zeolite A is around 1.1 million metric tons per annum making it the " globally preferred detergent builder". Many western countries are the major user of zeolite A as a builder. In India, SPIC, Chemicals & Plastics and NALCO produce this zeolite A with plant production capacity of 10,000 tpa each. The present detergent demand in the country is estimated to be around 90,000tpa. Considering 15% of the detergent builder in it, there is a 135000tpa demand for detergent builder in India. Presently in India, only a few detergent powders manufacturers like Henkel, Procter & Gamble are using zeolite A as builders, others are using STPP due to higher cost of Zeolite A. However, with environmental regulations becoming more stringent, the change over to zeolite is going to be in future which will trigger the demand for zeolite A. Production of zeolite A at a competitive price to STTP can shift the balance in favor of zeolite- A.

CONCLUSION

As the availability of kimberlite waste is high, approach to develop multi – product from this material was adopted and 3 products were developed. Process know – how for production of sodium silicate, zeolite A for detergent grade application and precipitated silica for rubber compounding has been developed at laboratory and pilot scale (10 kg batch scale) studies have been done.

From these studies, it is evident that kimberlite can be converted to variety of value added products namely MgO, Red mud, Sodium Silicate, zeolite A, precipitated silica, zeolite Y, and Molecular sieves adsorbents. In view of the availability of huge quality of kimberlite, it is prudent to have multi – product portfolio using same equipment with variation in process condition only.

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