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SILICA BASED INDUSTRIES - FUTURE PROSPECTS

Proceedings of a Seminar Held on 13th September 1996

Organized by Natural Resources, Energy and Science Authority of Sri Lanka
47/15, Maitland Place
Colombo 7.

Foreword

I consider this seminar a great success, because of the involvement of many participants from Industry. This may be due to the theme 'Silicate Based Industries -Future Prospects' which is an industrial topic. During the last three years we have invited industry to take part in seminars, workshops and other NARESA activities without much success. But the representation from industry at this seminar has been encouraging. NARESA has been the major focal point of funding basic and applied research for many years and almost all grantees are from Universities or Government Institutions.

At most of the seminars scientists come up with brilliant ideas and suggestions but very few of these are put into action. The industry must play a major role in implementing any new findings. Academics are limited to their publications without a sponsor or an investor. Therefore it is time that industries and universities come together hand in hand for the development of this country.

Technology and basic science should go together. Technology plays a major role in every industry, but in Sri Lanka the basic research aspect is lacking in industry. NARESA would be in a position to play a major role to improve the bond between Industries and Universities.

During the recent past NARESA has been receiving more money for research. Joint projects which come from an Industry and an University/ Institute could receive support from NARESA by helping them with monitoring and even with providing funds!

The theme of this seminar is very important to Sri Lanka since industries based on Silica have been established in Sri Lanka for a long time. We have to be more careful of using a nonrenewable resource like Silica. There should be a clear understanding of how we should use our nonrenewable raw materials. The guidelines should come from scientists. NARESA could take necessary action to implement these by interacting with the Government.

Professor Priyani E. Soysa
Director-General, NARESA

LIST OF PARTICIPANTS

Resource Persons

Prof. O.A. Ileperuma	Department of Chemistry, University of Peradeniya.
Dr Bandula Perera	Ceylon Glass Company Ltd., 148, Maligawa Road, Ratmalana.
Mr Nimal Ranasinghe	Geological Survey & Mines Bureau, 4, Senanayaka Bldg., Dehiwala.
Mr Sarath Silva	Ceramic Research Centre, Piliyandala.

Committee Members

Prof. H.D. Gunawardhana	Department of Chemistry, University of Colombo, Colombo.
Prof. V. Kumar	Department of Chemistry, University of Peradeniya, Peradeniya.
Prof. M.U.S. Sultanbawa	89/1, Dickman's Road, Colombo 5. (Chairman, Steering Committee on Chemical Sciences)

Invitees

Prof. Lal Fernando	University of Moratuwa.
Dr M. Ismail	CISIR, 363, Bauddhaloka Mawatha, Colombo 7.

Participants

Mr K.D. Amarasena, CISIR, 363, Bauddhaloka Mawatha, Colombo 7.
Dr A.M.M. Amirudin, CISIR, 363, Bauddhaloka Mawatha, Colombo 7.
Mr J.P.A. Chandralal, Ceramic Research Centre, Lanka Ceramics,Colombo 2.
Mr Priyantha Deraniyagala, Ceylon Glass Company Ltd., 148, Maligawa Road, Ratmalana.
Dr S.A. Fernando, Department of Chemistry, University of Colombo, Colombo
Mr K.A. Gunawardena, Royal Ceramics Lanka Ltd., 51/1, Fife Road, Colombo 5.

Dr J. Handawela, 12/52A, Perera Mawatha, Kotuwegoda, Rajagiriya
Dr(Mrs.) S. Hewage, Department of Chemistry, University of Colombo,Colombo
Prof. B.S.B. Karunaratne, Department of Physics, University of Peradeniya, Peradeniya.
Mr S.W.A.P. Kulartna, Ceylon Glass Co.Ltd., 148, Maligawa Road, Ratmalana.
Mr D.R.K. Lokuliyana, CISIR, 363, Bauddhaloka Mawatha, Colombo 7.
Mr P. Manokeran, Siedles Industrial Agencies (Pvt.) Ltd., 150,Ward Place, Colombo 8.
Mr P.P. Manoranjit, NERD Centre, Indsustrial Estate, Ekala, Ja-ela.
Mr R.A.D. Padmasiri, Kaolin Refinery, Lanka Ceramics Ltd., Borelesgamuwa.
Dr K.S.D. Perera, Chemistry Division, Open University, Nawala, Nugegoda.
Mr T.T.R. Peiris, Ceylon Glass Co.Ltd., 148, Maligawa Road, Ratmalana..
Mr Aruna Perera, Siedles Industrial Agencies (Pvt.) Ltd., 150, Ward Place, Colombo 8.
Mrs S. Ranatunga, CISIR, Bauddhaloka Mawatha, Colombo 7.
Mr N.P.P. Ratnayaka, Ceylon Glass Co. Ltd., 148, Maligawa Road, Ratmalana.
Mr J.K.A. Sirinatha, Royal Ceramics Lanka Ltd., 51/1, Fife Road, Colombo 5.
Mr Rex Stewart. Ceylon Quartz Industries (Pvt.) Ltd., No. 65, Braybrook Place,
Mr Eraj Wijesinghe, Ceylon Quartz Industries (Pvt.) Ltd., No. 65,Braybrooke Place, Colombo 2
Mr W.H.S. Wijerathna, National Paper Company,

SEMINAR ON "SILICA BASED INDUSTRIES - FUTURE PROSPECTS"

Date : 13th September 1996
Venue: NARESA Auditorium

PROGRAMME

9.00 a.m.	-	9.15 a.m.	Registration of participants
9.15 a..m.	-	9.30 a.m.	Welcome Address **Prof. Priyani E. Soysa** Director General, NARESA
9.20 a.m.	-	9.30 a.m.	Introductory Remarks **Prof. M.U.S. Sultanbawa,** Chairman, Steering Committee on Chemical Sciences
9.30 a.m.	-	9.50 a.m.	Occurrence of Silica Deposits in Sri Lanka **Mr Nimal Ranasinghe** Geological Survey & Mines Bureau
9.50 a.m.	-	10.00 a.m.	Discussion
10.00 a.m.	-	10.20 a.m.	Use of Silica in the Glass Industry **Dr Bandula Perera** Ceylon Glass Company
10.20 a.m.	-	10.30 a.m.	Discussion
10.30 a.m.	-	10.50 a.m.	Tea

10.50 a.m.	-	11.10 a.m.	Use of Silica in the Ceramics Industry **Mr Sarath Silva** Ceramic Research Centre
11.10 a.m.	-	11.20 a.m.	Discussion
11.20 a.m.	-	11.40 a.m.	Silica as a Raw Material for the Future **Prof. O.A. Illeperuma** University of Peradeniya
11.40 a.m.	-	11.50 a.m.	Discussion
11.50 a.m.	-	12.00 noon	Concluding Remarks **Prof. H.D. Gunawardhana** University of Colombo

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INTRODUCTORY REMARKS

Prof M.U.S. Sultanbawa

The Director General of NARESA, participants at this seminar on Silica based industries and guests, I take great pleasure in welcoming all of you for the seminar. The success of silica based industries depends on an appreciation of the existence of two types of raw materials for the growth and development of our industry.

(a) Industry based on renewable resources - these will therefore based on agricultural products on which the industry is based. Here the raw material can be an agricultural resource or an agricultural by-product. The product has to be produced efficiently as an agricultural resource. Besides another resource would be on agriculture by product which needs to be developed as a resource material for another material that is made for development of the country.

(b) In establishing an industry using a resource material which cannot be grown as for agriculture products. There are a number of other considerations which have to be collated and analysed before such a decision is taken.

(i) The total amount of raw material in one or more locations

(ii) How readily it could be gathered

(iii) Is it a surface material or one that is available below the surface.

(iv) The maximum amount of material that can be extracted per annum so that factory can function for a profitable period.

(v) In the utilization of such resources the maximum amount that should be processed per year should be decided by local technologists and scientists.

(vi) There should be local specialists included in panel that decides the consumption of raw material per annum.

(vii) In the extraction of raw material procedures for removal of dust particles, removal of stagnant water and other environmental damage should be taken care of.

The utilization of silica for a variety of purposes is well known. Any industry starting now should plan for integration and expansion in due course. This should allow the industry to function on a profitable basis for a period of 40 - 50 (?) years. During this period other activities like import of raw materials, sophistication of products by venturing into new areas of specialised product manufacture should be borne in mind so that the continuation of the already developed site can be continued and sustained for a longer period. Various speakers will speak of the different aspects of the industry and let me indicate some of them in brief outline.

Silica is a common name for the compound silicon dioxide (SiO_2). Quartz is silica in the shape of six-sided crystals commonly colourless and transparent but also at times found in yellow, brown, purple, green and other shades. White sand is pure silica, brown sand, containing impurities. It is an impure variety of quartz. Silicon is the second most abundant element in the earth's crust, and its compound silica, is a very common substance.

Silica is an inactive, water insoluble compound. It has a high melting point (ca 1710° C,) is transparent to UV light and expands only slightly with each degree increase in temperature.

At high temperatures silica joins with aluminium oxide, sodium carbonate and calcium oxide forming silicate. It reacts with Hydrofluoric acid, forming SiF_4 and with carbon or powdered magnesium in an electric furnace. It can be reduced to the element silicon by reducing agent carbon in an electric furnace.

Silica is used as an abrasive, it is used in mortar, concrete and in glass making. Quartz is used in making optical instruments, laboratory apparatus and specialities as radio crystals.

Soluble silicates include sodium and potassium silicate. Sodium silicate solutions (water glass) is used as an adhesive, for fireproofing cloth, preserving eggs and for making silica gel.

Commonly clay is produced by weathering feldspar. Feldspar is a compound of K, Al and Silicon Oxides.

White clay is kaolin, used for making chinaware. Bricks are baked clay. Impervious coatings on bricks are obtained by melting. The outside surfaces (vitrifying) or by melting common salt onto the surface. Pottery is made from mixed clay, moulded and baked, forming biscuit ware. The glaze is then applied and ware fired again. Dissolved metallic oxides, give colours. Tableware is a special type of pottery made from clay, feldspar and ground silica. The glaze and pattern are applied as for pottery. Porcelain is pottery that is fired at a higher temperature than ordinary chinaware. Porcelain is used for laboratory ware. Enamel ware is glass-coated iron ware.

To form Portland cement, shale and limestone are heated in a rotary kiln, forming a clinker; this product and gypsum added to catalyse setting. Cement sets with addition of water only. Concrete is made from cement, crushed stone and sometimes it is reinforced with steel.

Glass is made from sand, soda and cullet to aid in moulding. There are many special types of glass. Fabricating is accomplished by making.

(I) sheets drawn or cast

(2) jars and bottles blown into molds.

Colours in glass are due to dissolved oxide or colloidal suspension of metals. Borosilicate glass has high silica and boric oxide content. Optical glass contains lead and potassium silicates. Safety glass is (a) plate glass sandwiched into wire reinforcement or (b) glass plate sandwiched with a plastic material between them.

Different speakes will be expanding on the areas that have been outlined by me. Thank you.

OCCURRENCE OF SILICA DEPOSITS IN SRI LANKA

Nimal Ranasinghe

1. INTRODUCTION

Considering the abundance of elements within the earth's crust, silicon (Si) is found to average nearly 290,000 parts per million and is the second most abundant element. Oxygen at 473,000 parts per million is the most abundant element. In comparison, the third most abundant element is aluminium which is only 81,000 parts per million. Silicon rarely or almost never occurs in its elemental form in nature. It occurs as silica (SiO_2) or as silicate (SiO_4) and its many polymorphs. It is therefore the most common mineral commodity on earth.

Basically, silica occurs in two forms; in the free state and as silicates. The latter forms the basic building blocks of the largest rock forming families of minerals. In this note, focus will be only on silica which occurs in its free state.

2. MINERALOGY

In considering the silica group of minerals we find these have structures consisting of three dimensional lattices of SiO_4 tetrahedra where all four oxygen are shared by adjoining tetrahedra. Natural silica glass lechatelierite is an exception. The main polymorphs of silica are shown in Fig. 1.

3. MAJOR FORMS OF SILICA

Three major forms of silica are noted. They are,

a) Quartzite
b) Vein quartz (Silica quartz)
c) Silica sand

(a) Quartzite

Quartzite occurs in Sri Lanka forming significant relief features in many parts of the country. Prominent among them is the Sudukanda ridge in the Polonnaruwa / Giritale area which continues up to Trincomalee. They are also very common in the highland areas (Fig. 2). This is an impure form of silica found generally as coarse, granular or massive whitish rocks. Unlike in other rocks no foliation or bedding is noted. The impurities in quartzite contain iron stains due to weathering of iron-rich minerals such as magnetite. Pitting within quartzite is quite common and are due to weathered feldspars.

Despite the wide occurrence of quartzite, due to the presence of impurities they have so far not found any use in mineral based industries. SiO_2 grade of common quartzites vary from 70% to 90%. As the reserves are immense if an appropriate industry could be established its future would be very bright indeed.

(b) Vein Quartz

Sri Lankan vein quartz are noted for its high grade (purity) where SiO_2 values are in the region of 99.9%. These are found mainly in the central highlands associated with Precambrian crystalline rocks. Notable deposits are found at Galaha (Ranasinghe, 1987), Akarella near Opanayake Pelmadulla, Ratnapura, Rattota and Mahagama near Embilipitiya, Sigiriya etc. Fig. 3 shows currently known locations of vein quartz. The deposits at Ambalamana, Akarella and Rattota are being mined.

The proved reserves of quartz in Sri Lanka are not available but inferred reserves of vein quartz of high purity is considered to be over 20 million tons, particularly within the deposits at Ambalamana and Akarella (Herath 1995). These deposits usually occur as boulders, some glistening white, pale pink, and greenish brown due to growth of moss and fungi. These boulders which are discontinuous present difficulty in proving their reserves as it is difficult to interpret sub surface, extent, shape and continuity. Reserves however, could be proved using core drilling but this is quite an expensive exploration technique.

(c) Silica Sand

In comparison to previously mentioned forms of silica i.e. quartzite and vein quartz which are found associated with Precambrian crystalline rocks, silica sand or glass sand occurs within the Quaternary deposits and are less than one million years old. Best known deposits occur in the Madampe, Marawila, Nattandiya areas.

Within this area, three deposits can be recognized. Namely, Madampe, in the north, Kudawewa in the middle and Marawila-Nattandiya in the South (Herath 1995). The deposits extends to about 10 km. and average about 100 m in width. Their average thickness is about one metre. In most areas they are found on the surface where most of the land consist of coconut estates.

Silica sand occurs also in the Ampan Vallipuram area in the Jaffna Peninsula. It occurs in a series of sand dunes lying about 1 km east and northeast of the Point-Pedro Ampan road. The dunes are well developed and reach a maximum height of about 50 feet east of Kudattanai. It is reported that these dunes extend over several hundreds of hectares and reserves as substantial. However, these sands which are a mixture of fine, medium and coarse grains are badly graded and carry iron staining which is difficult to remove by usual physical processes of mineral dressing. It is therefore, not very suitable for the manufacture of medium quality glass.

Small deposits of silica sand have been reported at Chavakachcheri near the railway station, Ekala and Borupana Ratmalana.

USES

The uses of silica varieties are directly related to their grades (purity). Pure forms of quartzite and silica sands are used in the manufacture of glass, ceramics, chemicals and fluxing agents. Due to its high heat resistance it is used as foundry sand in the manufacture of moulds and cores for casting metals. It is also used as abrasives, filteration media, construction sand and gravel. It is used as a filler in paint, plastics, rubber, adhesives, putty, caulks and sealants. Precipitated silica with very fine particle sizes are used as anti-slip agents, carriers, liquid thickener and clarifier, food, pharmaceuticals, chemicals, fertilizers, desiccant and flatting agent in paint. The high grade silica which is used for the production of fused silica leads to the manufacture of optical lenses, mirrors, windows, and semiconductors. Super pure silicon are used in integrated circuits, solarcells, infrared optical systems and optical fibres. Silicones are used as lubricants, water repellants, moisture proofing and electrical insulations. High grade silica is now increasingly utilized in high-tech electronic industry.

Ferrosilicon is used as de-oxydising and alloying agent.

The world capacity of silica sand is in the range of 150 million tons and ferrosilicon/ silicon about 4 million metric tons of contained silicon. Marketing conditions are that silica sand steady, silicon increasing and ferrosilicon decreasing (Harben, 1995).

LOCAL INDUSTRIES

Main users of silica locally are the ceramic and glass industries. These are ideal examples of an industry which utilizes local material and manufacture a product which has both local and export markets. At present, there are few exporters of silica quartz in the raw form under special BOI and cabinet approval. As a policy, allowing of minerals to export in the raw form is discouraged. It is encouraging to note that several joint venture partnerships to manufacture products using silica are now under consideration and expected to come on stream in the very near future.

SUMMARY

1. The quartz deposits of Sri Lanka consist of

   a. Silica sand
   b. Vein quartz (Silica quartz)
   c. Quartzite

2. Silica sand is found within the Quaternary deposits, whereas, vein quartz and quartzite are associated with Precambrian rocks.

3. a. The main deposit of vein quartz which are mined are at Owella - Kaikawela and Ambalamana - Galaha.
   b. Smaller deposits are found near Balangoda, Embilipitiya and Sigiriya areas.

4. Considering the availability of high grade vein quartz and its potential use in the high-tech industries, this mineral commodity could provide substantial assistance to the National Economy, and industrial prominance to Sri Lanka. Therefore, to allow export of vein quartz in the mineral (raw) form would only jeopardize the country's development.

References

1. Harben, P.W., 1995, *In The Industrial Minerals Hand Book*, 2nd Ed., Metal Bulletin Plc, London, pp 156 - 161.

2. Herath, M.M.J.W., 1995, *In Economic Geology of Sri Lanka*, 5th Ed., Ministry of Industrial Development, Sri Lanka, 216 pp.

3. Ranasinghe, N.S., 1987, Vein Quartz Survey of Ambalamana - Galaha unpub., *Internal technical reports*, GSMB.

SILICA GROUP OF MINERALS

Have structures consisting of 3-dimension lattices of SiO_4 tetrahedra where all four oxygen is shared by adjoining tetrahedra. Exception is natural silica glass: lechatelierite.

There are three main polymorphs silica °

° Quartz (∝ or low quartz) common quartz — Stable up to 573° C; Trigonal Trapezohedron

* Coloured varieties

Purple -	Amethyst
Brown -	cairngorm -smoky quartz
Yellow -	citrine
Pink -	rose quartz
White -	milky quartz
Clear -	rock crystal

° Quartz (β or high quartz) — Stable 573 - 870°C; Hexagonal trapezohedron

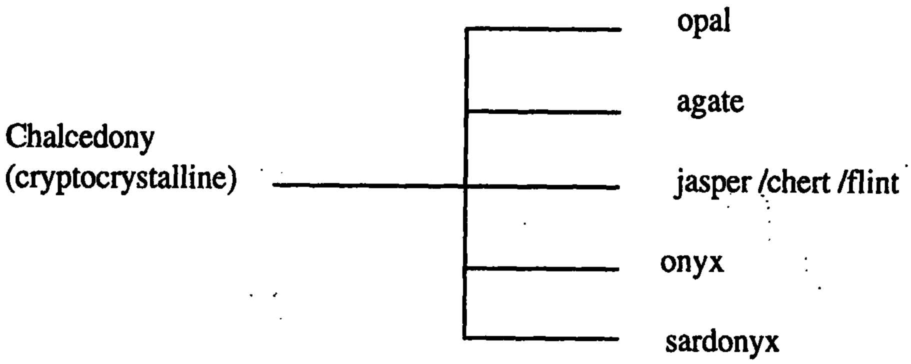
° Tridymite — Stable above 870° C; Hexagonal holohedral

° Cristobalite — Stable at 1470° C; Cubic

Coesite — high pressure (20 Kb); monoclinic

Fig. 1

Fig. 1 continued



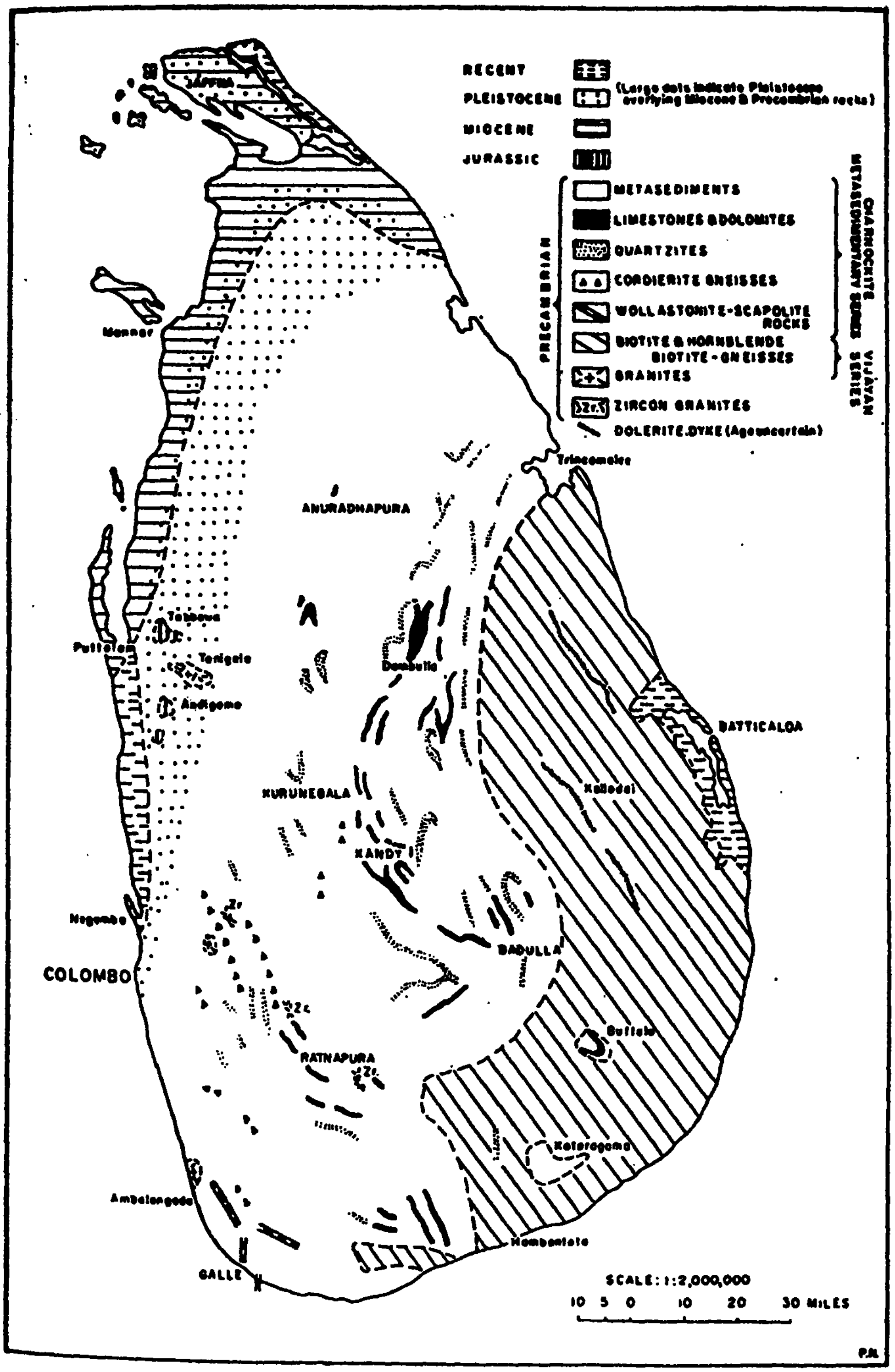
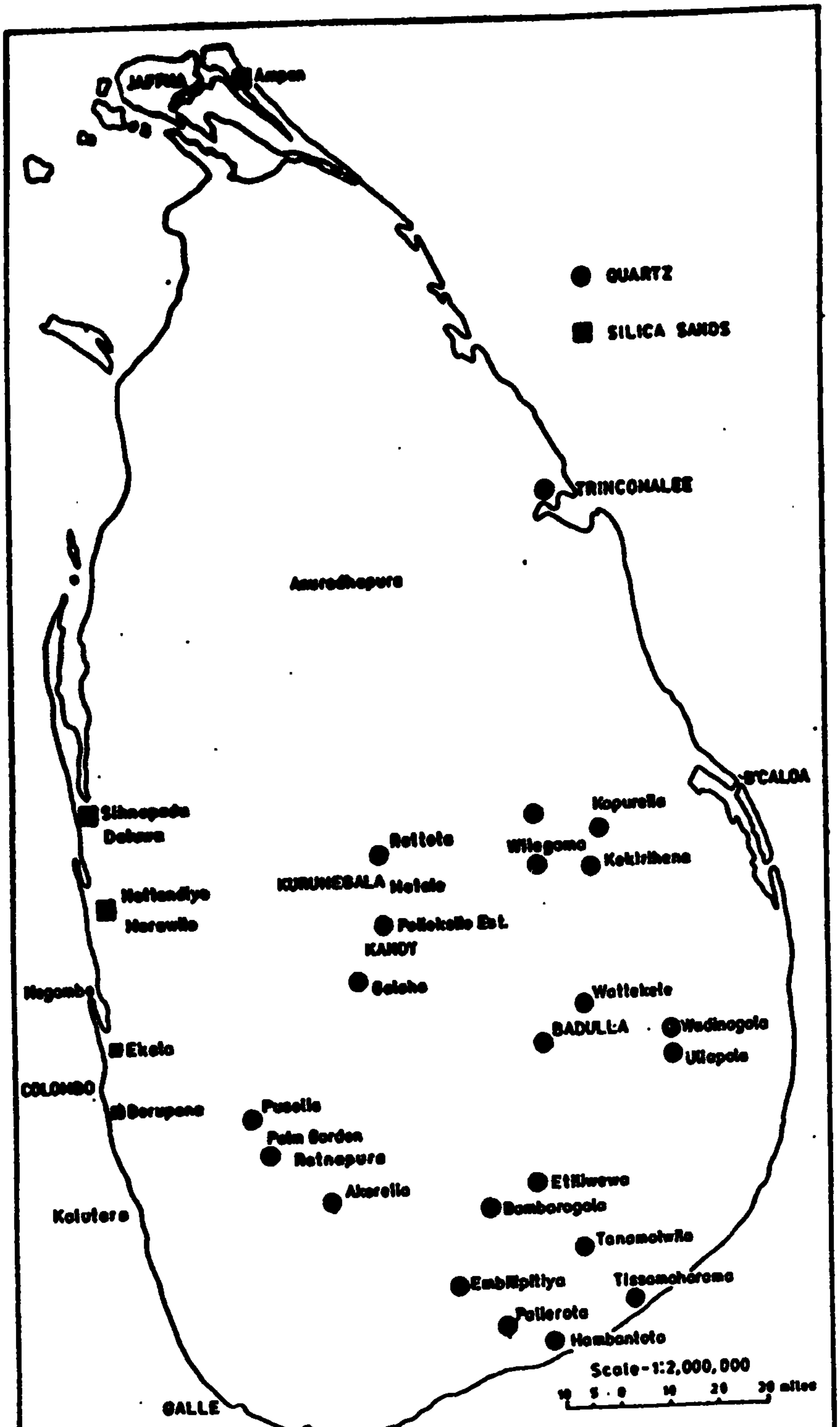


Fig. 2 GEOLOGICAL MAP — SRI LANKA



OCCURRENCES OF VEIN QUARTZ AND SILICA SANDS — SRI LANKA

Fig. 3

USE OF SILICA IN THE GLASS INDUSTRY

By Dr C. T. S. B. Perera

Glass is not a solid. It is a super cooled liquid. In making glass, silica is melted into a glassy matrix using sodium carbonate and other natural additives such as Dolomite, Calcite, Feldspar in case of Soda Glass (better defined as Soda Lime Glass). This is the type produced in greatest proportions by tonnage of all glasses produced in the world.

Then there are glasses that are referred to as Boro Silicate glass where boric oxide is added to the batch. There are various other types of glasses including crystal glass, heat resisting glass, optical glass etc.

Glass is formed from "Glass formers", glass modefiers and fluxes to give a random network structure. Glass formed are the oxides of silicon, Boron and phosphorus. Sometimes Arsenic and Germanium are also used as formers. These are ions with high ionic potentials, forming very strong bonds with oxygen. Glass modefiers or "Network modefiers" are of relatively low ionic potential such as alkali or alkaline earths. The glass thus formed as a melt once cooled down does not crystalize on account of it's high viscosity which increases to such an extent that it behaves as a solid.

Silica in glass industry is one of the most important raw materials. In Sri Lanka silica is available for industrial usage in two forms -

(a) Silica Sand
(b) Quartz

Silica sand is usually associated with high iron contents (in form of illmenite) and can be separated by gravitation methods and electromagnetic separation. Container glass (Flint) should have an overall iron content (Fe_2O_3) less than 0.06%. Silica sand which has Fe_2O_3 content of around (0.1%-0.15%) can be purified to low iron levels of around 0.02% by the above methods.

In addition to the chemical purity, particle size of the sand and other raw materials are very important. Normally silica sand should be less than 30 mesh (500 μ). This is because large particles will not melt properly and give rise to serious problems such as unmelted particles in the finished product. The fines are restricted to 5% less than 0.125 mm. Present day glass melting furnaces are extremely sophisticated and highly thermally efficient. The regenerators or checkers of the furnace which function as the escape for exhaust gases as well as heat exchangers for secondary air will get seriously damaged by fine particles that are released from the chargers. This will not only shorten the life of the furnace but will also reduce the efficiency and the output of the furnace over long periods.

Extremely pure Quartz are available in Sri Lanka. Quartz of lower purity associated with high purity Quartz can be used in container or sheet glass production. However, high purity quartz has been found to be suitable for manufacture of Crystal Glass and even optical glass as far back as 1987. It was recommended by Czechoslovakian authorities in 1987 that Sri Lanka quartz by using only dry magnetic separation could provide standard crystal glass making silica while only Chemical Bleaching was required to use this to produce optical glass.

USE OF SILICA IN THE CERAMIC INDUSTRY

Mr Sarath Silva

1. INTRODUCTION

Silica raw materials have various functions in ceramic masses and products. They act as a filler and also principal glass former or carrier of refractoriness if fired in a pure form. More than 96% of the quality silica mixed into masses in the ceramic industry is derived from quartz sand and vein quartz. Silica raw materials categorised as non-plastic raw materials in ceramic industry.

Silica sand and quartz are found in abundance in Sri Lanka. Quartz deposit of high purity have been identified in Kaikawala and Elahara in Matale district, Galaha in the Kandy district and Balangoda. Silica sand is available in Marawila - Nattandiya area.

2. OCCURRENCE OF SILICA

Silica occurs naturally as vein quartz, silica sand, sandstones quartzite, flint pebbles and as semi precious chalcedony, opal and agate.

3. CHEMICAL COMPOSITION

There are three main crystalline forms of silica, Quartz Cristabolite and Trydimite. All have same chemical formula SiO_2. Vein quartz in Sri Lanka is very pure and contain 99.8% of SiO_2. Silica sand has purity of 97% - 98% where as quartzite contain 96 - 96.5% of SiO_2. (Table 1)

Flint is used as a source of silica where high purity is not essential. A typical flint contains 85% of SiO_2.

4. COLOUR, DENSITY AND HARDNESS

Vein quartz occur as transparent crystals, milky white or white grey masses. The density of colourless crystals of natural quartz at room temperature is 2.65 g / cm^3. The hardness of quartz crystal is 7 (Moh's hardness scale).

TABLE I

CHEMICAL ANALYSIS OF SILICA RAW MATERIALS USED IN CERAMIC INDUSTRY

Constituent	Vien Quartz	Silica Sand	Quartzite
SiO_2 %	99.82	98.7	96.5
TiO_2 %	0.001	0.02	n.d
Al_2O_3%	0.003	0.35	1.71
Fe_2O_3%	0.002	0.03	0.18
MgO%	0.01	traces	0.05
CaO%	0.01	traces	traces
Na_2O %	0.002	n.d.	0.34
K_2O%	0.004	n.d.	
LOI %	0.16	0.28	0.25

In cristobalite and tridymite the atoms are less closely packed than in quartz, hence they show lower specific gravity.

Cristobalite 2.32
Tridymite 2.28

Quartz and silica sand are the most common silica raw materials for ceramic industry.

5. PARTICLE SIZE AND OTHER PROPERTIES

In many ceramic bodies, especially in structural clay products, quartz grains of sand sizes (0.25 - 0.125 mm) are commonly acceptable. In chinaware, sanitaryware and similar products finely ground form as silica flour is used. Another application of silica flour is for glazes and frits, which must be ground iron free and SiO_2 content should be over 99%. To achieve these conditions, usually vein quartz is used.

Quartz flour and quartz sand act in ceramic mass primarily as a filler, they lower plasticity, dry shrinkage, firing shrinkage and deformation, the time of drying and also the shock strength of the fired bodies. Also silica gives strength to the bodies during firing. Quartz in a finely ground state and in distinct amount is the principal glass former of ceramic products at higher temperatures.

Coarse sand grains or an excessive content of quartz in the mass may cause dilatation of the body during firing.

Each ceramic product needs constant grinding conditions of the quartz and other raw materials. So that texture of the body remains constant.

The silica raw material, silica sand, quartz, gravel, quartzite, chert and silex are mostly used in structural clay products where as their very finely grained species and varieties are used mostly in the manufacture of refractory silica.

SILICEOUS ROCKS - FLINT AND SILEX

Flint and Silex consist of finely crystalline silica or chalcedony.

FLINT

Flint pebbles are used as grinding media in the iron free grinding. The choice of the maximum pebble size depends on the mill diameter and the speed of revolution of the mill aggregate.

SILEX

Silex bricks are used as mill lining material. Find grinding of ceramic non-plastic raw material is usually done in ball mills and the ground product has to be iron free for use in ceramic bodies and glazes. For this reason the wear surface of mill lining consists of silex bricks. Flint pebbles which are also iron free are used as grinding media.

IMPORTANT INVERSION TEMPERATURES

There are three main crystalline forms of silica, quartz, trydymite and cristobolite and also these three forms undergo minor structural changes know as inversions. The main inversions which occur are as follows:

$$\alpha\text{ - Quartz} \quad 573^\circ\text{ C} \rightleftharpoons \quad \beta\text{ - Quartz}$$

α - Tridymite 117-163° C $\rightleftharpoons$ β - Tridymite

α - Cristobolite 230-280° C $\rightleftharpoons$ β - Cristobolite

Most important of there in ceramics is difference in thermal expansion.

When α - Quartz changes to β - Quartz there is a linear expansion of 0.45%.

Cristobolite changes produce an expansion of about 1% and Tridymite inversion involves 0.1% linear expansion.

At these inversion temperatures size changes occur very quickly. There rapid changes in size can lead to cracking during firing if the temperature is taken up or dropped too quickly through the inversion temperatures during firing.

THERMAL EXPANSION OF BODIES AND GLAZES

An important non crystalline form of silica is fused silica. Fused silica formed by heating any form to above the melting point and then cooling. Fused silica has a very low and almost linear thermal expansion and has good thermal shock resistance.

Due to the presence of fluxes, silica in glazes melt at low temperatures than its normal melting point and form a glass with the other material of the glaze. the higher the silica content of the glaze, it forms more fused silica and lower its thermal expansion.

Silica content of the body composition increases, the thermal expansion of the body also increases. This is because it does not all enter to the glassy phase on firing.

Specially in the porous bodies, where the proportion of glass formed in the biscuit is small, shows higher expansion.

When the different in thermal expansion of the body and the glaze is more, crazing may result.

SILICA REFRACTORIES

Silica Bricks - Silica bricks are used mainly as a steel plant refractory where they form the roof of open hearth furnaces. They are also used in coke ovens and in the roofs of glass furnaces.

Their outstanding properties are

1 - The ability to withstand loads at high temperatures
2 - High resistance to attack by iron oxides and alkalis
3 - Freedom from shrinkage even at operating temperatures of 1600° - 1700° C
4 - Good thermal shock resistance above 600° C

LIME SAND BUILDING BRICKS

Lime sand bricks are made with lime, silica sand and water as raw materials by hydrothermal hardening in autoclaves. These bricks consist of 85 - 90% by weight of sand. The grain size distribution of the sand has an important influence on the amount of lime required to achieve the compressive strength of the bricks. The fine fraction of less than 0.1 mm should not be more than 10%.

SPECIAL CERAMICS

SILICON CARBIDE

Silica Carbide is an exceptional material for use at very high temperatures.

Silicon carbide is formed by reacting silica sand with ground, low-ash coke.

$$SiO_2 + 3C \rightarrow SiC + 2\,CO$$

The conversion is done in batchwise. The silica sand has to meet following requirements.

Grain Size   0.1 to 0.5 mm

SiO_2 -   99.5%

Al_2O_3 -   0.2% (for black Silicon Carbide)

The coarsely crystalline Silicon Carbide is sieved, ground, cleaned by magnetic separation and other chemical processing. Silicon carbide is used in the abrasives refractories and electrical industry and also used in the foundry and steel industry.

SILICON NITRIDE

Silicon Nitride is an important material for engineering applications. It has good mechanical properties. Its dimensional stability and oxidation resistance when subjected to temperatures upto 1400° C is excellent. Also material has good thermal shock resistance and high electrical resistivity. Due to these properties Silicon Nitride is used for high temperature gas turbines, crucibles, thermocouple sheaths, platforms and supports and in the semi conductor industry. Also in the nuclear-energy field, silicon nitride has extremely useful applications.

MAJOR USES

In ceramic industry for ceramic bodies, frits and glazes.

eg.

1. Heavy clay industry
2. Earthenware
3. Sanitaryware
4. Porcelainware
5. Bone chinaware
6. Stoneware
7. Electro porcelainware
8. Refractory Industry

ELECTRICAL AND ELECTRONIC INDUSTRY

In addition to above, high purity quartz are used in the production of fused silica. Quartz crystal is a piezo-electric material which forms the basis of quartz resonators used widely in quartz watches, computers and microprocessors for frequency control and also in quartz filters for wave band selection in communication devices.

High purity quartz is used to produce quartz filters, for selection wave bands of radios and televisions and also used in telecommunication equipment, watches and clocks and in microprocessor circuits for personal computers and military and industrial machinery.

Fused silica is manufactured by fusing high purity silica sand or quartz crystals. Fused silica is an important material for production of fibre optic cables. Fused silica find increasing application in the electronics and related industries.

The other important use of fused silica is in the production of silica crucibles. Low thermal expansion and high resistance to thermal shocks are some of the properties of silica crucibles.

SILICA AS A RAW MATERIAL FOR THE FUTURE

Professor O. A. Ileperuma

Silicon is one of the most abundant elements in the earth's crust (27.75%) and second only to oxygen in overall abundance. Despite the ubiquitous nature of silicate minerals, silicon was not isolated until the 19th century when Berzelius used potassium to reduce K_2SiF_6.

$$K_2SiF_6 + 4K \rightarrow Si + 6KF$$

The production of high purity silicon has become important since it is used in an enormous variety of electronic devices. Large scale production of silicon is achieved by reduction of quartz with carbon at 1700 °C.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

Both silica sands and crystalline quartz are employed as the source of SiO_2. However, for the production of electronic grade silicon, crystalline quartz is preferred owing to its low impurity content. Coke is the preferred form of carbon which is obtained by heating coal in coke-ovens, but there is also the possibility of using coconut charcoal for this purpose. Pure quartz is mixed with oil-coke and placed in huge squat steel cylinders having diameters of about 10 m. This steel cylinder is cooled by water from outside. Several graphite electrodes are used for electric heating of the charge. A large current and a moderate voltage are employed for the heating process. The reaction is started by short circuiting the electrodes with small graphite electrodes underneath the pile. Liquid silicon is tapped and run off periodically and the furnace is kept running continuously.

The product obtained in this manner is called metallurgical grade silicon with ca. 98.5% Si and the main impurities are Fe, Al, Ca and O (from quartz) and V, Mn (from coke). This is used directly to prepare organosilicon compounds.

The preparation of high purity silicon for use in the electronics industry can be achieved using several methods relying on the formation, purification and reduction of compounds such as SiF_4, $SiHCl_3$ and SiH_4.

I. Reaction of metallurgical grade silicon with HCl

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

ii. Purification of $SiHCl_3$ (b.p. 31.8° C) by distillation

iii. Chemical vapour deposition of semiconductor Si by reduction

iv. Single crystal growth by Czochralski and zone refinement methods

In the Czochralski process, a seed crystal of silicon is used to draw large single crystals of silicon from a molten bath of refined silicon. The seed crystal attached to a wire is pulled with simultaneous rotation through the melt while the crucible holding molten silicon is rotated in the opposite direction. Single crystals of up to one meter in length and 15 cm in diameter can be obtained using this method.

Another method is the thermal decomposition of Na_2SiF_6 to give SiF_4 followed by reduction with Na to give SiF4 followed by reduction with Na to give a mixture of NaF and Si. Leaching of NaF by acid gives high quality Si. Recently SiH_4 has been used to obtain high purity polycrystalline rods.

The polycrystalline Si is next converted to single crystal silicon. In the Czochralski method a seed crystal is used to draw single crystals from molten Si. Single crystals of over 1 m in length and 15 cm in diameter can be obtained using this method.

In the zone refining method, only a small band of silicon rod is melted at any time and the molten zone is moved along the length of the rod and the impurities dissolve preferentially in the molten phase and are drawn to the end of the rod and single crystal growth continues as the melting zone is moved. The float zone method can be applied more than once to increase purity.

Silicon and silica constitute the starting materials for a number of high and low technological processes producing materials for a wide range of applications and some of these are discussed below.

1. QUARTZ CRYSTALS

These are used for optical instruments and quartz resonator plates for frequency control which are essential for modern communication systems. They are usually grown from alkaline silicate solution. Other important starting materials of silicon include silicon tetrachloride and sodium silicate.

$SiO_2 + CCl_4$ or $(PCl_3) \rightarrow SiCl_4$

Na_2SiO_3 is obtained by melting sand with soda ash at 1450° C

$Na_2CO_3 + SiO_2 \rightarrow Na_2O.n\ SiO_2 + CO_2$

Na_2SO_4 and carbon can also be used for this purpose.

Na_2SiO_3 can be obtained by dissolving sand in caustic soda.

Transparent vitreous silica is produced from quartz crystals and the non-transparent ones from glass sand with electrical heating using carbon electrodes in a furnace. Slow cooling results in quartz glass which is resistant to a wide variety of chemicals. It is used in optical instrumentation, for high temperature chemical reactions and windows for UV detectors. There are numerous advances in the chemistry of materials based on silica. Thus silicones produced by the reaction of alkyl halides with silicon have a wide variety of applications. Silica gel produced by the hydrolysis of silicon tetraethoxide produces "silica gel" which is used as a drying agent and a chromatographic material.

Sol-gel synthesis of extremely fine particles of silica give "aerogels", which are extremely light and have very good insulating properties. Hydrolysis of tetraethylsilicate under hydrothermal conditions give extremely light aerogels having very low electrical and thermal conductivities. Thus these materials are suitable as insulating materials, for example, in refrigerators and since silica is non-polluting it can be conveniently recycled without any environmental damage. High silica zeolites such as ZSM-5 (Mobil oil) are active as selective catalysts in carrying out a large number of organic synthesis.

2. FERRO-SILICON

Crude silicon can be used directly to produce ferro-silicon alloy; however, the preferred method is the reduction of quartz and scrap iron with coke.

$$SiO_2 + Fe + 2C \rightarrow FeSi + 2CO$$

Ferrosilicon constitutes the laminated core of transformers and also used in AC transmission lines.
Silicon is also alloyed to aluminium to increase strength and used for example in aircraft ladders.

3. SILICON CARBIDE

Silicon carbide is manufactured by the reduction of quartz in the presence of an excess coke.
The reactions involved are:

$$SiO_2 + 2C \rightarrow SiC + 2CO$$

$$Si + C \rightarrow SiC$$

It has a high mechanical strength (9.5 on the Mohs scale) and chemical stability. It is used as an abrasive. When pure, SiC is an intrinsic semiconductor but may be doped with various impurities to give extrinsic semiconductors. β-SiC is also used as a high temperature semiconductor.

4. APPLICATIONS IN PHOTOVOLTAICS AND MICROELECTRONICS

Large scale utilization of solar cells is still prohibitively expensive but the impending energy crisis and the rising costs of other energy sources will certainly increase the demand for silicon solar cell panels in the future. With a share of 0.01% , solar energy plays only a minor role in the electricity production globally producing just about 400 MW of energy. The US Department of Energy predicts that by the year 2030, the sun will furnish roughly 240,000 MW of electricity, roughly 600 times the current amount.
The computer revolution would not have been possible but for the development of superchips made from silicon based semiconductor materials. A tiny chip could store information contained in 1000 pages of a book.

In the fabrication of solar cells, silicon single crystals, boron and phosphorus are usually added as doping agents to produce p and n type semiconductors. A thin wafer of p type semiconductor about 300 microns thickness is doped at one end to a thickness of about 0.2 microns by phosphorus to make it n type and hence obtain a p-n junction device. Metal contacts which is usually a Ti/Ag alloy is applied and heat treated at 600° C to give good electrical contact. An antireflection coating of silicon monoxide (SiO) is then applied on the surface. Several such wafers are interconnected by soldering metal stripes in a solar panel.

5. SYNTHETIC AMORPHOUS SILICA

Synthetic amorphous silica is prepared by either flame hydrolysis of silicon tetrachloride or by the hydrolysis of sodium or calcium silicates. These silica particles have extremely small sizes and have hydrophilic surfaces owing to the presence of hydroxyl groups on the particles. If methyl silicon chlorides are hydrolysed, hydrophobic silica particles are obtained. These are useful in the plastics industry, as catalyst supports, as insulating materials and even for removing toxic fumes in the atmosphere. It is used in the paint industry as a thickening agent and also as a water repellent.

6. SILICONES

Silicon or silicon-copper alloy reacts with alkyl halides at elevated temperatures to give mixtures of alkyl silanes.

$$2CH_3Cl + Si/Cu \quad (300^\circ C) \rightarrow \quad (CH_3)_2SiCl_2 + Cu$$

These compounds can be separated and purified by distillation. Hydrolysis of these chlorosilanes give silanaols which undergo further condensation to give polymeric compounds having Si-O-Si linkages. By using different starting silanes, polymers with very different properties are obtained. If methyl groups are present they give silicone oils which are resistant to higher temperatures compared to hydrocarbon oils. Silicone rubbers are composed of very high molecular weight units bridged together with ethylene groups. These rubber products are oil resistant and can be used at high temperatures when compared to normal rubber materials.

7. SILICA GEL

Silica gel is obtained by acidifying silicates. The gel contains large amounts of water held in a cage like structure. When this is heated water is driven off resulting in "silica gel". It is a drying agent and a support for many catalysts. It is also used as a column material for chromatographic separations.

Discussion

This section summarizes the outcome of the discussions that took place during the seminar and the concluding remarks made by Prof. H.D. Gunawardane.

Responding to a question on how to minimize wastage during mining and whether the miners could be educated, Mr Nimal Ranasinghe stated that the Mines Bureau gives training and instructions for miners, but very few people are interested to undergo training. It is very difficult for the Bureau to monitor the mining procedures in individual mines. The miners have to get what they want for export within their time limit and the lower quality materials are just thrown away. To minimize wastage high tech machinery which can utilize even poorer quality materials should be used. On the other hand, if there is a market for material which is now considered as waste, eg. ferro- silicates, then wastage would be minimised. When utilizing a nonrenewable resource the whole resource must be used. Processing of raw materials should be developed with the latest technology. But it must be done soon, or else by the time the technique is available the material may not be there to be utilized.

Dr Bandula Perera explained that rather than exporting raw silica which ultimately will be crushed to micron scale particles before further processing, the materials can be value added by just simple crushing. If we cannot develop our own technology we should invite developed countries to start industries to develop our own raw material, and ultimately that technology transfer will benefit the country.

Universities and industries should work together to improve the research and development. The National Chambers of Industries, can play a major role here. It is important to involve young graduates fresh from the university, if one wants to develop new ideas.

Prof Ileperuma stated that participants at the seminar should make maximum effort to implement ideas that would make improvements to the industry and the country's need.

Concluding Remarks
Prof. H.D. Gunawardena

Technology and Science should co-exist. Technology cannot survive without a basic knowledge of the sciences. Science and technology should interact with industry, but this is lacking today. For example, the Eppawala apatite deposit which was discovered 26 years ago is not being utilized properly, and Sri Lanka is still importing fertilizer. This nonrenewable resource could be utilized for a number of generations. A suitable industry should be started to fulfil country's fertilizer need and this should be planned very carefully. Inviting big foreign companies to exploit the resource could lead to exhaustion of the raw material within a few years. This would be a national disaster!

In conclusion, Prof. Gunawardane put forward following ideas which came out from the seminar for further consideration:

1. Even a small scale industry could be economically viable if it was properly planned. For this to be a success, legislation should be prepared and, most importantly, implemented.
2. Value addition for exported raw material should be done.
3. There should be greater involvement of basic science aspects with the industry. A separate centre should be formed to initiate and promote University-Industry cooperation.