

# **THE USE OF SALTERN BITTERNS FOR MANUFACTURING MAGNESIA REFRACTORIES.**

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### **ABSTRACT**

In Srilanka there are salterns where bitterns are produced as potential magnesia compounds , from which magnesia can be precipitated , consolidated and heat treated under certain conditions to produce high quality magnesia pellets which are of similar quality to that produced in the U.K. This is confirmed by the microscopical , chemical and X-ray diffraction studies. This research describes the recovery of magnesia in the lab scale using the sea water bitterns ,from Hambantota salterns , which is presently discarded.

### **Introduction**

The term basic refractories is used to describe refractory materials that react as chemical basic materials at high temperatures and therefore resist attack by alkali , and lime rich fluxing materials. Magnesia is one such material which can be recovered from the bitterns. The major application of basic refractories is in the steel industry as a lining material for basic steelmaking processes including the steel refining. Furthermore , significant basic refractory consumptions are taking place in lime kilns , cement kilns , glass tank regenerators and the refining of nonferrous metals.

### **Sources of High grade Magnesia for Refractory Manufacture**

Salterns are the potential magnesia sources in Srilanka. Refractory grade magnesia could be produced from these salterns. This research deals with the production of such high grade magnesia pellets from the discarded bitterns.

### **Salterns**

There are four major salterns available in Srilanka as sources of magnesia raw materials for the manufacture of basic refractories. At the present moment this valuable raw material ( Bittern ) is discarded into the sea. The approximate tonnage of bitterns produced in Srilanka is about 100,000 tons per year with the production

### Precipitation and Drying

Magnesium salts from the bitterns were precipitated by the addition of ( 1 : 1 ) ammonia solution into a 1000 cc bittern sample. A thick gelatinous precipitate was formed almost immediately. Alternative methods such as slaked dolomitic lime water could be used but the yield was not as good as that obtained with ammonia. The precipitate was filtered using BCRA vertical filter press. The filter cake was air dried in a fume cupboard for about 4 hours and subsequently oven dried at  $110^{\circ}\text{C}$  for 2 hours using a Gallenkamp oven. A sharp volume reduction of the precipitate took place during the drying process.

### Calcination of Magnesia

The above product was calcined in a gas fired furnace at  $1000^{\circ}\text{C}$  ( fig. 3 ). Thereafter it was ground in a ceramic lined mortar followed by sieving through 300 mesh B.S sieve. Immediately after sieving , the powder sample was stored in a desiccator as it was hygroscopic.

### Powder Pressing

The powder specimens prepared were subjected to washing with acetone for several times and the dry product was finally pressed uniaxially using a hand operated hydraulic press (Fig.4). A specially fabricated 15 mm diameter die was used for powder pressing. The load on the plunger was increased gradually from zero to 8000 kg , and maintained at this maximum load for 10 sec. before it was released. The powder compact sample was thereafter removed from the die in the normal way.

### Sintering of Magnesia

The sintering of the Magnesia pellets was carried out using the induction furnace as shown in ( Fig. 5 & 6 ). The sample of magnesia approximately 15 mm diameter and 3 mm thickness was carefully inserted via the feed system into the Alumina working tube coupled with a graphite succceptor. Power was supplied through the coil via a R.F generator while the optical pyrometer was used to measure the temperature inside the furnace. The current through the coil was gradually increased until the required temperature was attained (  $1900^{\circ}\text{C}$  ) , thereafter this maximum temperature was maintained for 10 seconds before cooling.

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points located at Palavi , Elephant pass , Puttalam & Hambantota. The analysis of the bittern from Hambantota is as follows :

#### **Bittern Analysis ( Hambantota )**

<u>Constituent</u>	<u>Percentage</u>
NaCl	16
MgCl <sub>2</sub>	6
MgSO <sub>4</sub>	4
KCl	1
NaBr	0
Water	72
	----
Total	99
	----

#### **Sample Collection**

The Bittern samples were collected from Hambantota salterns. The particular location was Mahalevaya ( Fig. 1 ) , where the bittern was pumped out and discarded from the salting out yard into the discharge pond. The sampling was done during a dry season when the harvest of common salt was taking place ( Fig. 2 ).

#### **Experimental procedure**

The samples of bittern collected were subjected to the following :-

- (i) Precipitation of Magnesia in the form of Magnesium hydroxide from the liquor using ammonium hydroxide (1:1) .
- (ii) Calcination and Powder preparation.
- (iii) Uniaxial pressing into tablets.
- (iv) Sintering using an Induction Furnace.
- (v) Microstructure determination.
- (vi) X-ray analysis.



### Microstructure Examination

After cooling , the samples of sintered Magnesia pellets were mounted in araldite in the usual way. The vacuum technique was adopted while mounting the specimens into specimens holders. The polishing of the specimens for microstructural determination was carried out using the silicon-carbide powder of various grades starting with the coarsest grade initially. The final polishing was done using 6-micron and 1-micron diamond paste in that order using the laps.

The microstructure examination was done using Vickers microscope with a photographic camera attachment , and thereafter the two specimens , viz : Srilankan magnesia and Steetley ( U.K ) magnesia pellets were compared.

### X-Ray Analysis

The samples of magnesia sintered at  $1800^{\circ}\text{C}$  ,  $1850^{\circ}\text{C}$  and  $1900^{\circ}\text{C}$  respectively, using the induction furnace were examined using pinhole transmission camera using Copper  $K_{\alpha}$  radiation . The variation of grain sizes at different sintering temperatures was studied from the spot sizes and the X-ray diffraction pattern was obtained corresponding to the maximum spot size.

### Results

The chemical analysis of the magnesia pellet using the classical chemical analysis shows the following :

<u>Composition</u>	<u>Percentage</u>
MgO	98.75
Fe <sub>2</sub> O <sub>3</sub>	0.75
Na <sub>2</sub> O + K <sub>2</sub> O	0.25
	-----
Total	100.00
	-----

The microstructural examination reveals that the magnesia produced from Srilanka bittern and Steetley (U.K ) magnesia are almost identical ( fig. 7 , 8 ) .

The X-ray diffraction pattern shows the presence of Periclase ( MgO ) lines as shown in the fig. 9 . It is also clear that there is a change in spot size of the magnesia grains as sintering progresses , with the maximum spot size occuring at  $1900^{\circ}\text{C}$  ( fig. 10 ).( Compare this with the spot size of Steetly magnesia fig. 11 ).

### **Conclusion**

The preliminary research into the recovery of magnesia from sea water bittern clearly shows that high grade magnesia refractories could be manufactured in Srilanka. The microstructure , X-ray analysis , and chemical analysis show that the properties of Srilankan magnesia are similar to Steetley Magnesia in the U.K.

### **Suggestion For Further Work**

I suggest that this research should be continued on a pilot scale..At the moment such facilities are not available in the University. Instead of using ammonia which is rather expensive , the possibility of using an other alkaline solution such as calcined dolomitic limestone in water should be investigated. Such a solution may impart impurities into the magnesia grains , causing physical and chemical property variations. The effects of these impurities on magnesia have to be studied. Further research should be conducted on magnesia brick specimens prepared from a pilot plant pellets , for its mechanical and high temperature properties, particularly Refractoriness Under Load, and Spalling tests.

### **Acknowledgement**

I wish to thank .Steetly Refractories of Great Britain for providing a sample of high grade dead-burnt magnesia for this research work.Thanks are also due to the Heads of Departments of Ceramics and Metallurgy in Leeds University for providing laboratory facilities to complete this research work.Finally, thanks are due to Lanka Salt Ltd for permitting me to collect bittern samples from Hambantota Salterns and also providing other technical information.

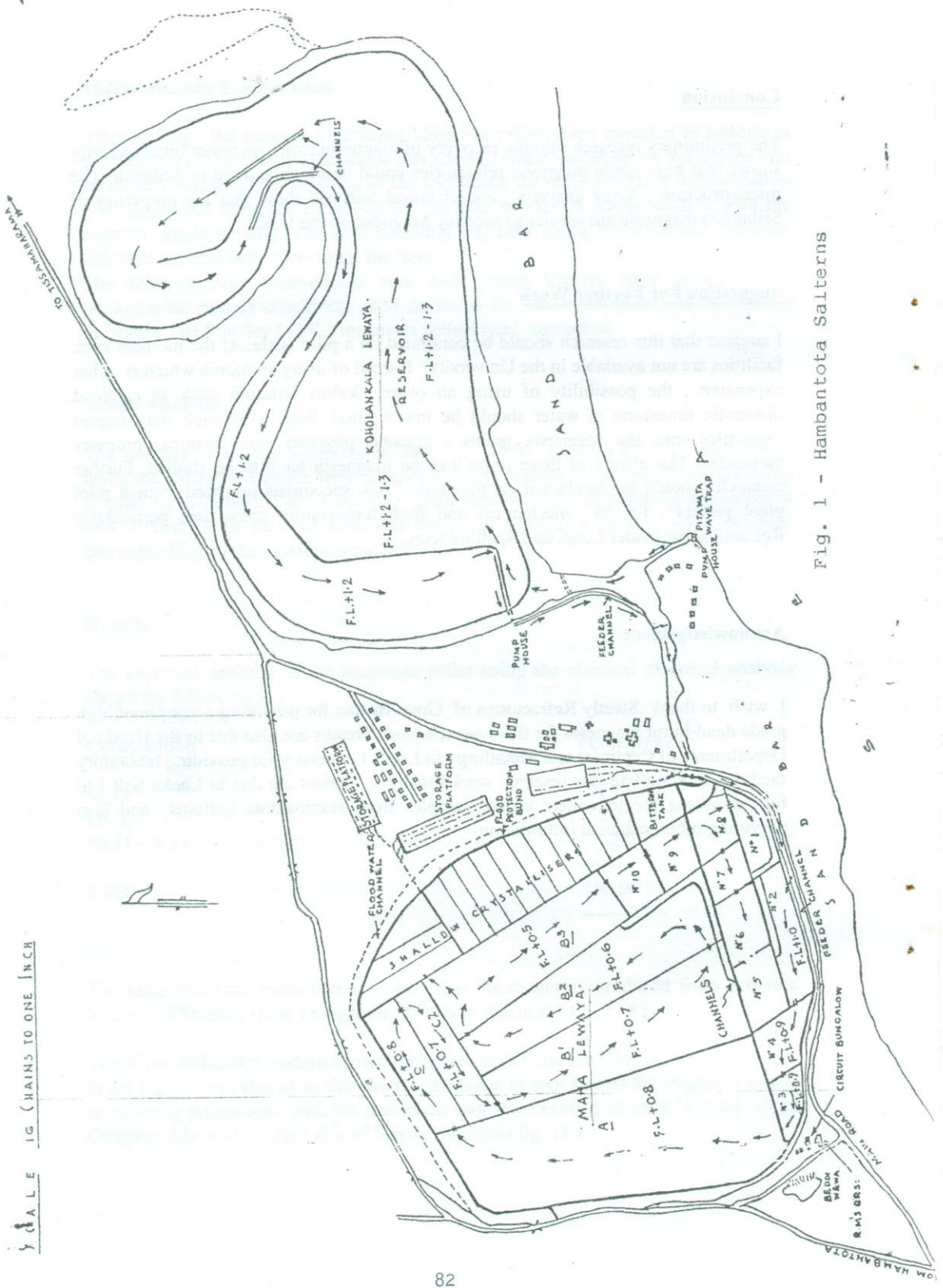


Fig. 1 - Hambantota Salterns

SCALE 1/4" = 1 CHAIN TO ONE INCH



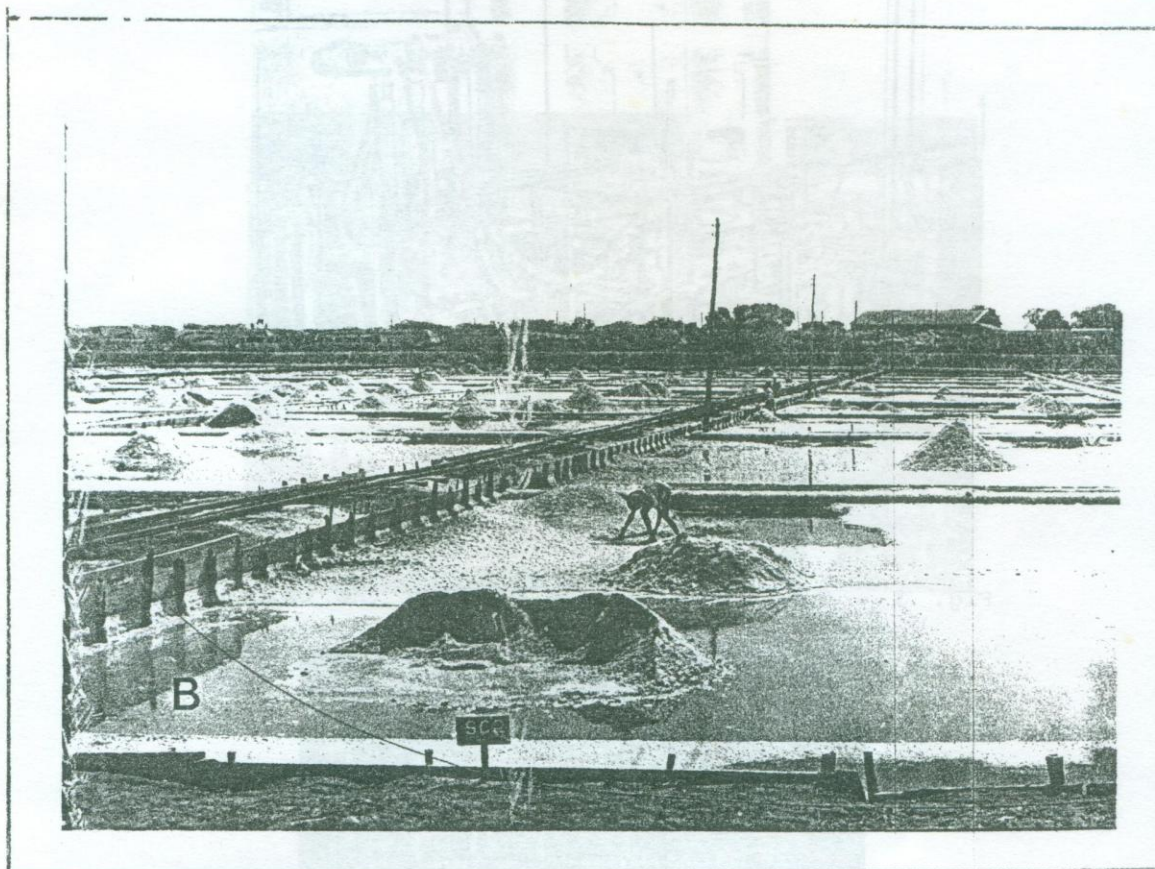


Fig. 2 - Harvesting Common Salt  
Note: B is the sample location.



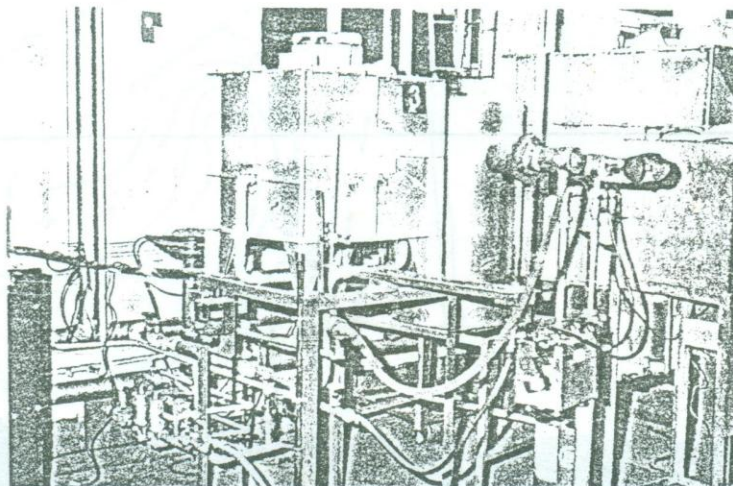


Fig. 3 - Gas fired furnace used in the calcination  
of Sri Lanka Magnesia Pellets

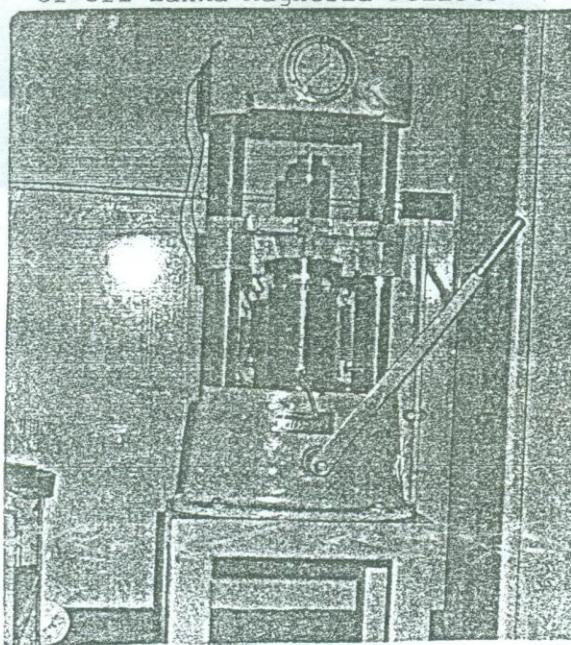


Fig. 4 - Hydraulic Press used in powder pressing

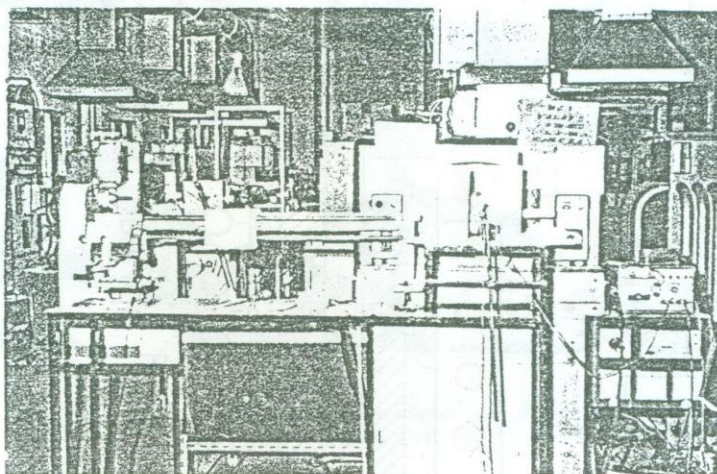


Fig. 5 - Induction Furnace used in the sintering of Magnesia Pellets.

NOTE - THE FEED SYSTEM ON THE LEFT HAND SIDE

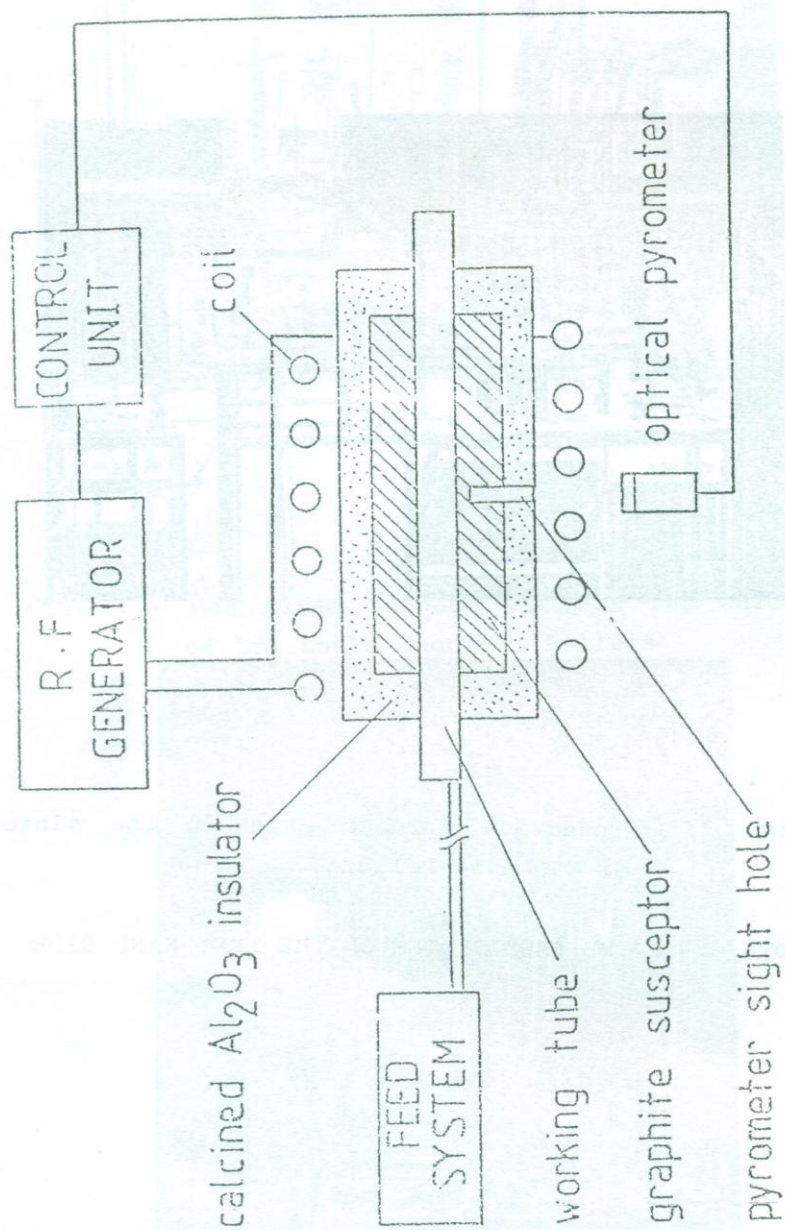


Fig. 6 - Induction Furnace (Layout)



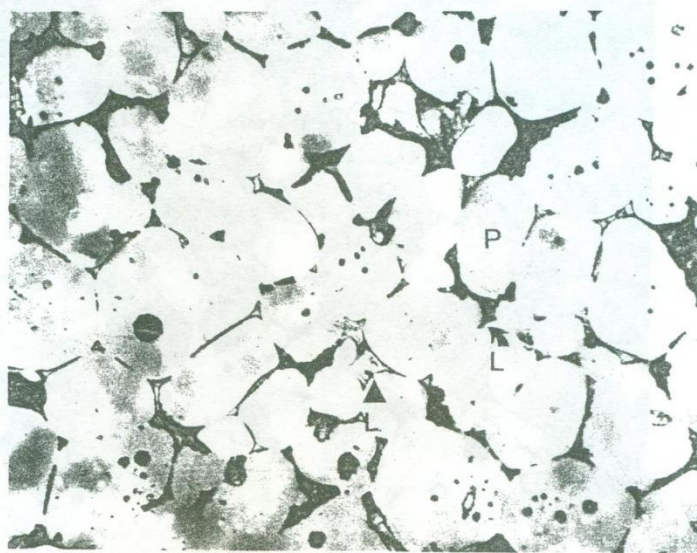
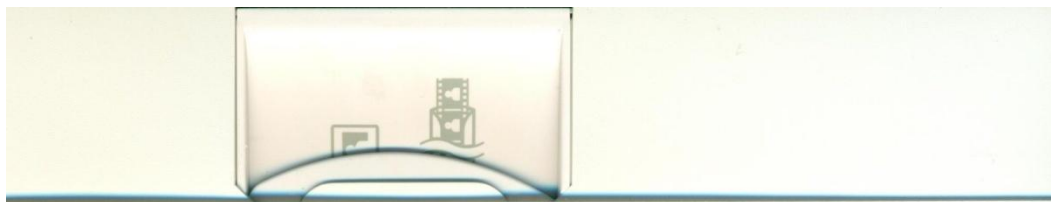


Fig. 7 (a) Optical Micrograph of Sri Lankan Magnesia Pellet. Mag. X 400 (Fired at 1900°C)

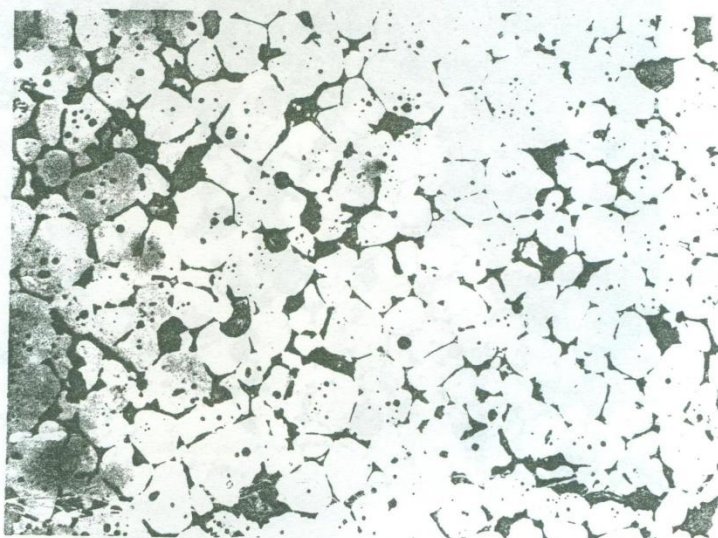


Fig. 7 (b) Optical Micrograph of Sri Lankan Magnesia Pellet. Mag. X 200 (Fired at 1900°C)

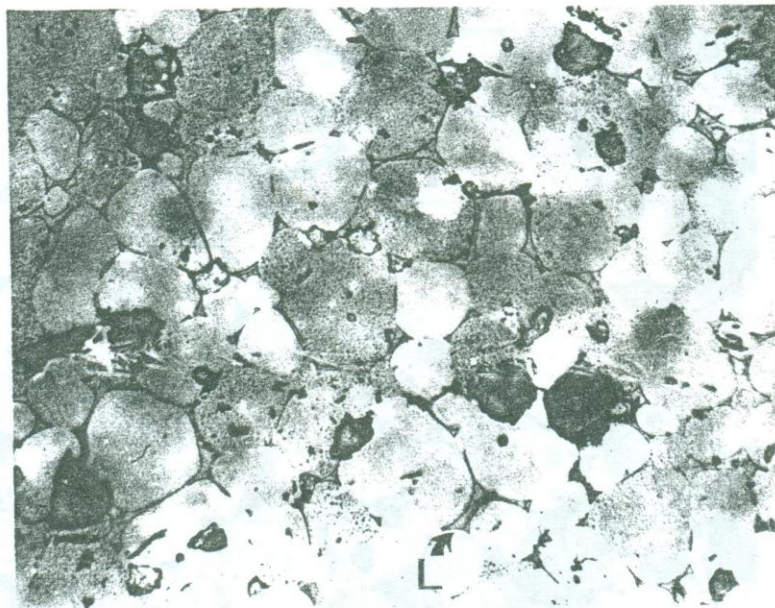


Fig. 8 (a) Optical Micrograph of Steetly Magnesia Pellet. Mag. X 400

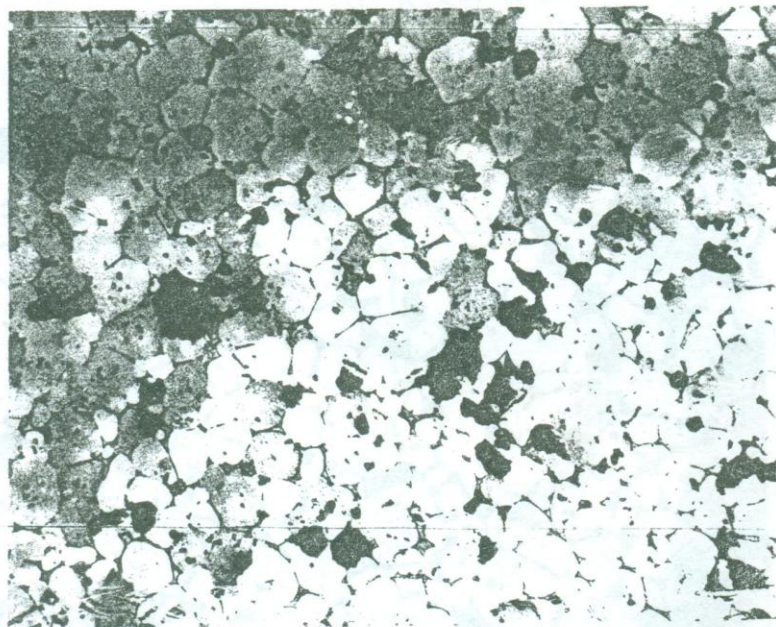


Fig. 8 (b) - Optical Micrograph of Steetly Magnesia Pellet. Mag. X 200



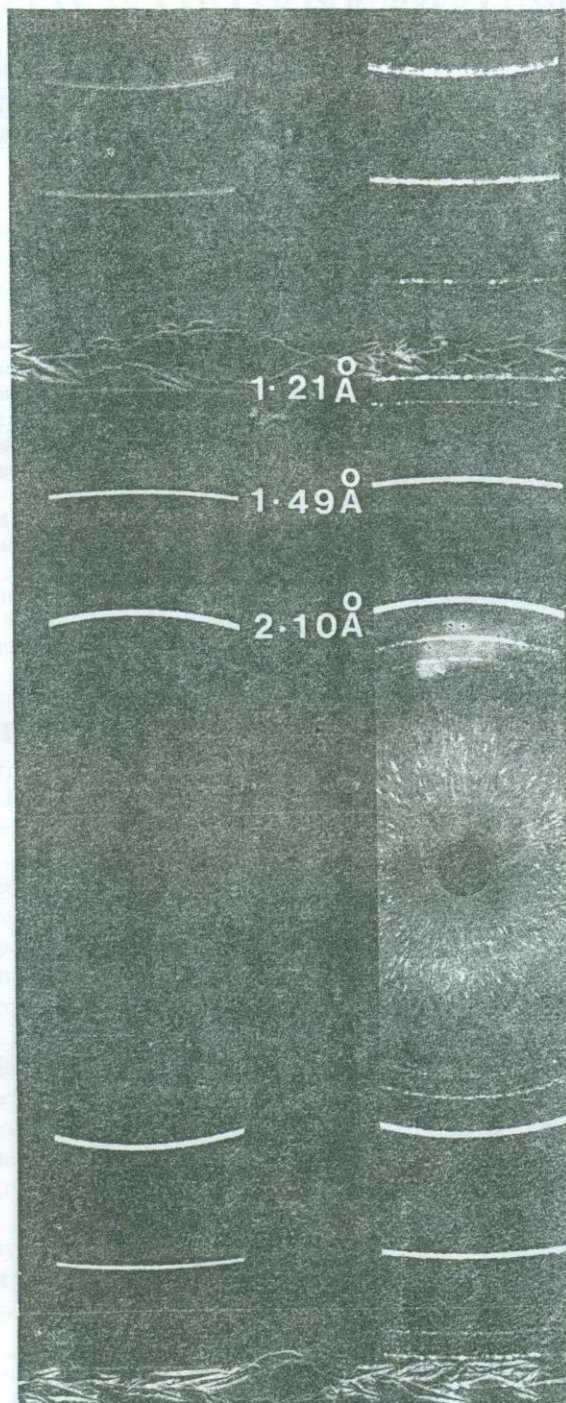


Fig. 9 X-ray Diffraction Patterns  
 R.H.S. - Sri Lankan Magnesia  
 L.H.S. - Steetly Magnesia  
 Note : The sharp Periclase (MgO) lines



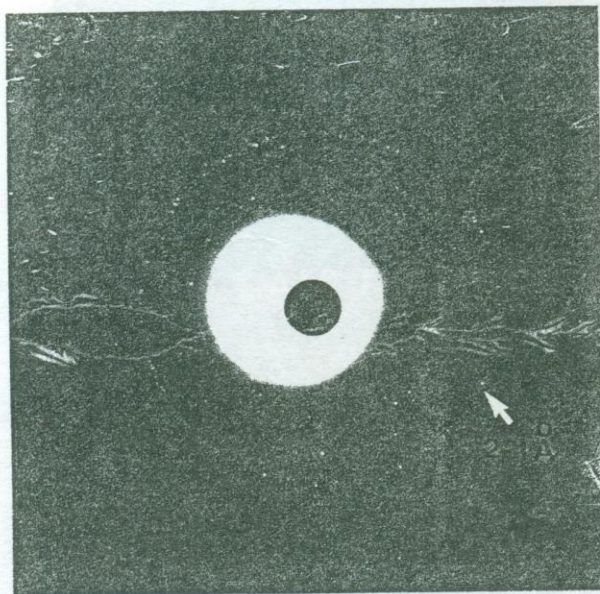


Fig. 10 - X-ray Pinhole transmission, Srilankan Magnesia

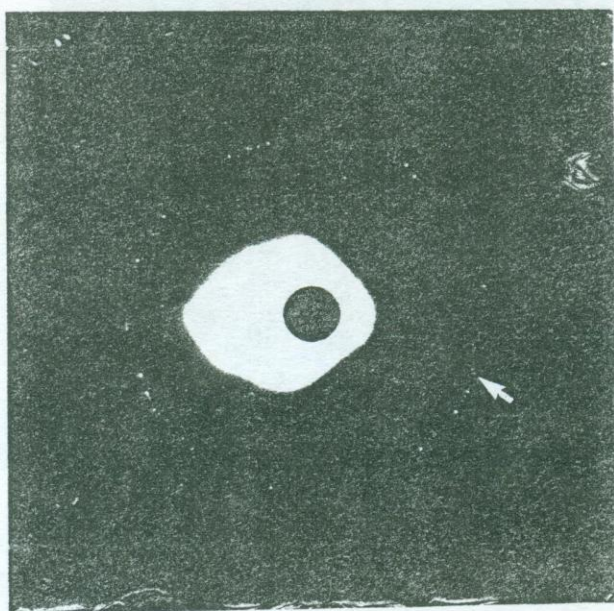


Fig. 11 - X-ray Pinhole transmission, Streetly Magnesia