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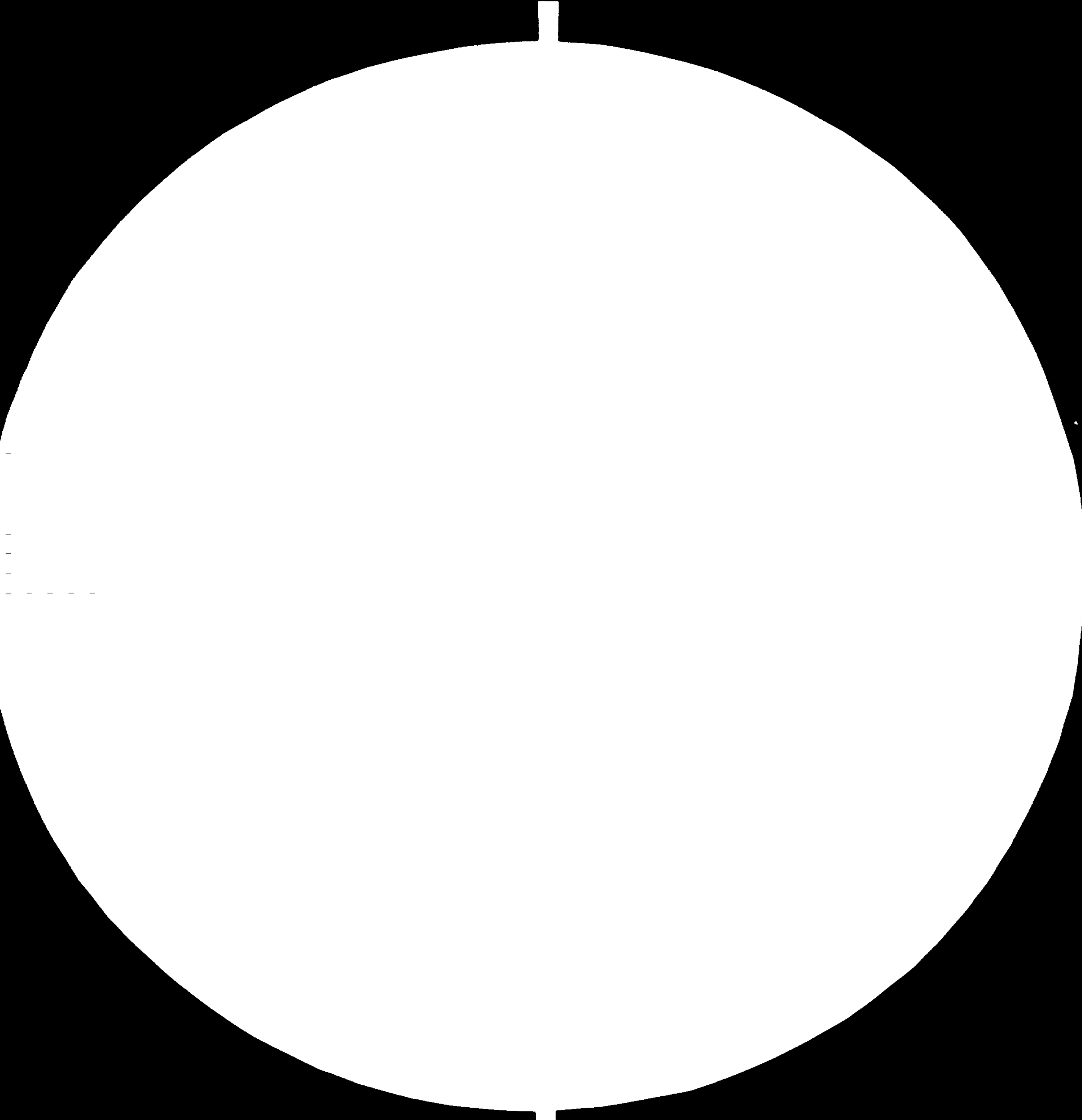

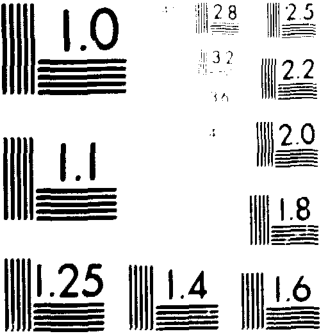
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DEPARTMENT OF
MINING & MINERAL ENGINEERING

THE UNIVERSITY OF LEEDS
ENGLAND

Restricted

21st October, 1980.

Development of Thai Dolomite for Basic Refractories

UNIDO Contract No. 77/112

UN-K-12624 - 380

Project findings and recommendations

Final Report prepared by:

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SUMMARY

The dolomite resources of Thailand have been surveyed and several surface deposits located. From their occurrence and nature some knowledge of the geology of Thailand has emerged. Several deposits were of excellent quality and equivalent to the best industrially-employed dolomites of Western Europe.

The dolomite industry, particularly in Europe, has been examined with especial reference to the conditions required for producing dolomite refractories and sea water magnesia from dolomites. The main user industries have been identified and the likely application in Thailand.

From the techniques which have been acquired, magnesia of +98% quality with a yield in excess of 97% has been produced under laboratory conditions from sea water from the Gulf of Thailand and Kanchanaburi dolomite. Ceramically-bonded bricks from Thailand dolomite have also been produced and these have been shown to have properties equivalent to the best European qualities.

A feasibility exercise has proved that dolomite refractories production will be viable in Thailand and will have considerable economic benefit. The production of sea water magnesia would be less favourable but the bitterns from sea salt production would form a more acceptable starting material. If agreement to supply other ASEAN countries could be reached large scale industries for both refractories and magnesia would be viable in Thailand.

ACKNOWLEDGEMENTS

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Special thanks are due to the Steetley Co. Ltd., Worksop, United Kingdom and to several of their senior personnel without whom much of the successful high temperature and large scale testing would have been impossible. Their contribution to feasibility studies based on vast experience was also invaluable.

We acknowledge also the help and friendly co-operation given by Dr. W. Munchberg, Dolomitwerke, Wulfrath, West Germany, Herr Helmut Merker of Trier Kalk, Mr. Christian Jacques of Produits Dolomitiques de Merlemont, Belgium and Dr. G. Allard of Dolomie Francaise and many others.

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CHAPTER I

INTRODUCTION

The name dolomite is given to minerals which are solid solutions of the carbonates of calcium and magnesium and to rock formations which are essentially composed of these minerals. An alternative name used to describe many formations is magnesian limestone.

Dolomites are formed in marine environments by precipitation and sedimentation in a similar fashion to limestones. Although they are not as common in occurrence as calcium carbonate deposits, dolomites occur widely in many parts of the world, but only relatively few are of commercial significance.

The rock forms can vary from soft (similar to chalk) to very hard (as is limestone) and they contain varying amounts of impurities which are associated with the sedimentation cycle. The hardest dolomites are of value as aggregates but for other industrial applications only those deposits which are low in total silica, alumina and iron oxide are acceptable.

Dolomites are used in many industries such as agriculture, glass-making, industrial fillers, chemicals etc. but the most important applications are as a basic refractory for the iron, steel and cement industries and as a precipitant of magnesium hydroxide from sea water, the product of which (as magnesia) is itself a refractory vital to the steel and other high temperature industries.

Without basic refractories, the modern steel industry could not exist. Hence dolomite has an important role in industrial society and good deposits of it are in considerable demand.

The science and technology of basic refractories are complex and, even if good quality raw materials are available, to convert them into a suitable form for industrial use requires a detailed knowledge of their properties and expert manufacturing techniques. For these reasons, basic refractories of all types, although widely used, are manufactured only in a few centres and there is considerable international trade in these commodities. Many countries have indigenous iron, steel and other industries requiring high temperatures but import virtually all their basic refractories.

THAILAND INDUSTRY

The iron and steel industries have been developing rapidly in Thailand during the past ten years. The steel industry is by far the major user of basic refractories and the present consumption for construction and repair of the furnaces is estimated at more than 15,000 tons annually valued at more than 150 million bahts (£3.5 x 10^6). Other industries requiring basic refractories in their operation include cement, ceramics and glass. With further expansion of iron and steel to meet the annual consumption growth rate of about 14 percent, increasingly large supplies of basic refractories will undoubtedly be required.

At present only alumino-silicate refractories are manufactured locally and all basic refractories are imported. Magnesite is generally preferred because of its high refractoriness and availability even though it has relatively low thermal shock characteristics. For many applications other basic refractories such as chrome-magnesite and dolomite can be used. A limited quantity of these are imported but so far none have been manufactured within Thailand from indigenous raw materials.

DOLOMITE IN THAILAND

Although the geological survey of Thailand is far from complete, it has been known for some time that there were dolomitic occurrences some of which were of high quality. It is now a legal requirement that all minerals, including aggregates, which are extracted in Thailand should be notified to the Department of Land, Interior. As a consequence and largely to facilitate and extend the geological survey, samples of potentially commercial minerals are sent to the Department of Mineral Resources (D.M.R.) in Bangkok for routine chemical analysis. It was from these and other records that dolomite was discovered in several parts of Thailand. Some occurrences were of potential good quality and were found in areas near to the established industrial centres for iron, steel, cement and ceramic manufacture. Others bordered the Gulf of Thailand with the potential of producing sea water magnesia.

Because of the high cost of importing basic refractories, principally from Japan, U.S.A. and Europe, the user industries approached the then Applied Science Research Corporation of Thailand (A.S.R.C.T.) to investigate the development of basic refractories in Thailand. These would be based on local raw materials and would replace the imported qualities. In addition to assessing the potential of dolomite as a refractory in its own right, the production of high grade magnesia from sea water using dolomite as a precipitant was also to be considered. An important aspect of the survey was to assess the commercial viability of such exercises in Thailand and to review the logistics in setting up manufacturing industries.

ESTABLISHMENT OF RESEARCH PROGRAMME

Within Thailand, there was neither the expertise nor the resources to investigate dolomite to the extent which was necessary. The United Nations Industrial Development Organisation was approached for assistance and through its help, preliminary surveys and assessments were completed which indicated that there was considerable potential.

Dr. R. W. Grimshaw visited Thailand and he recommended that a research programme should be established which would associate the work on dolomite with European industry, particularly the Steetley Co. Ltd., Worksop, U.K., and with the Department of Mining and Mineral Sciences, The University of Leeds.

In 1978, UNIDO awarded a research grant to second a research worker from the now Thailand Institute of Scientific and Technological Research (T.I.S.T.R.) to work full time on the dolomite project; part of the study to be geological and industrial surveys in Thailand and part to be based in Europe, particularly the U.K., examining fundamental aspects of dolomites and their firing behaviour in comparison with material already established as suitable quality.

SCOPE AND OBJECTIVES OF THE PROJECT

The work plan for the project was sub-divided as follows:-

1. To examine known deposits of dolomite in Thailand and from their study to elucidate the geology of the formations in relation to each other and to the general distribution of minerals.
2. If the geological study were successful, to predict where suitable quantities and qualities of dolomites are likely to be found in Thailand and hence to establish a "resource bank".
3. To compare the qualities of Thailand dolomites with other world sources of this mineral which are being used for industrial purposes. The qualities to be examined include not only detailed chemical analyses, but also physical properties, microstructures and crystallographic data.

4. To study the firing behaviour of Thailand dolomites again in comparison with European qualities to determine their suitability for the manufacture of pitch-bonded or ceramic-bonded refractories. In this context not only are high temperature properties of importance but also intermediate temperature characteristics to predict the probable behaviour in pre-firing in rotary or shaft kilns.
5. To assess the suitability of dolomites and also the sea water conditions around the Gulf of Thailand for the production of magnesia of high quality.
6. Provided that the results justified it, to consider the feasibility of a sea water magnesia and a dolomite refractory plant in Thailand. The study would take into account the probable indigenous requirements and also potential export markets. Very recently the latter aspect has assumed increased importance because of the extension of collaboration within the ASEAN community. Thailand could anticipate becoming the supplier of basic refractories to all countries within the community. India, Japan and possibly Australia all have export potential.
7. The feasibility study would also include plant design and costing and would, therefore, require that part of the research programme would be closely linked to British and other European manufacturers. At some stage it might be worthwhile to consider a pilot plant scale of operations in Thailand which would be based on the research findings.
8. Other uses for Thailand dolomite besides refractories would also be considered. These would include glass, filler and fertiliser industries.

9. To develop the technical capability of the T.I.S.T.R. in the field of mining, mineral processing and exploitation and in particular dolomite technology for carrying out research investigations into the potential utilisation of Thai dolomite as a basic refractory.

CHAPTER II

GEOLOGY AND OCCURRENCES OF DOLOMITE IN THAILAND

General Geology

The land mass of Thailand is unusual in shape and although political boundaries contribute, it is due in the main to geological factors. The country stretches in a N-S direction over 1400 mls. (2000 Km) but, over half its extent, the width in the E-W direction is under 100 mls. (140 Km). Thailand north of Bangkok and the Gulf of Thailand is mostly composed of alluvial deposits of recent origin from the rivers Chao Phraya, Mae Klong, Pasak, Mun and Mekong. In the extreme north the country extends into the foothills of the Himalayas but it is the eastern and western boundaries, particularly the latter, which dominate the country.

N-S ranges of mountains make up these boundaries. The eastern extremity is not impor tant in the present context because the Thailand boundary with Laos is the Mekong river and the mountains are mainly in Vietnam, Laos and Cambodia. There is a central small range of hills which are of interest in that they form the eastern seaboard of the Gulf of Thailand but the dominant feature is the western range which forms the Isthmus of Kra and ultimately the Malay Peninsula.

When the various locations of dolomite, the analyses of which were available in D.M.R. files and from other sources, were inserted on the map of Thailand there emerged a virtual continuous progression of this mineral along the "spine" of this western mountain ridge; there were also some reports of dolomite in the hilly region on the eastern side of the Gulf of Thailand and on one of the off-shore islands (Ko Si Chang).

In the early studies and subsequent field work on the project there emerged a tenable theory to account for the geological features of the "spine" or peninsula of Thailand.

Virtually all the formations of dolomite which have been identified and examined showed steeply-dipping, highly contorted strata. This was a feature around Kanchanaburi in the north, through deposits near to Ratburi and Phetburi (west of Bangkok), Prachuab Khiri Khan, Chumphon, Suratthani, Nakhorn Si Thammarat, and finally in the south in the region of Songkhla and Satun (Fig. II.1). The dolomite was not continuous because there were a multiplicity of faults, subsidiary anticlines, reverse folds and other geological anomalies but the trend was unmistakeable.

Various authors [2-6] have reported that in Thailand there is to be found a sequence of rock formations in the peninsula ranging from Ordovician, Silurian, Devonian, Carboniferous, Permian, Triassic to Jurassic in geological age. Because of pressure metamorphism and intense folding, deposits are frequently difficult, if not impossible to date because of the absence of fossils, but in general terms the sequence can be accepted. There are frequent igneous intrusions almost always to the centre of the "spine"; these are mainly granites or related acid rocks.

To the north of Ranong, the border between Burma and Thailand runs almost along the apex of the mountain ridge but to the south to the border with Malaysia near Songkhla/Satun the whole of the peninsula is in Thailand bordered by the Andaman Sea in the west and the Gulf of Thailand in the east.

It was this region which provided the most important clue to the geological structure. In this region, dolomite deposits of similar mineralogical appearance were found in both the east and the west separated by older deposits and in the centre by an igneous intrusion.

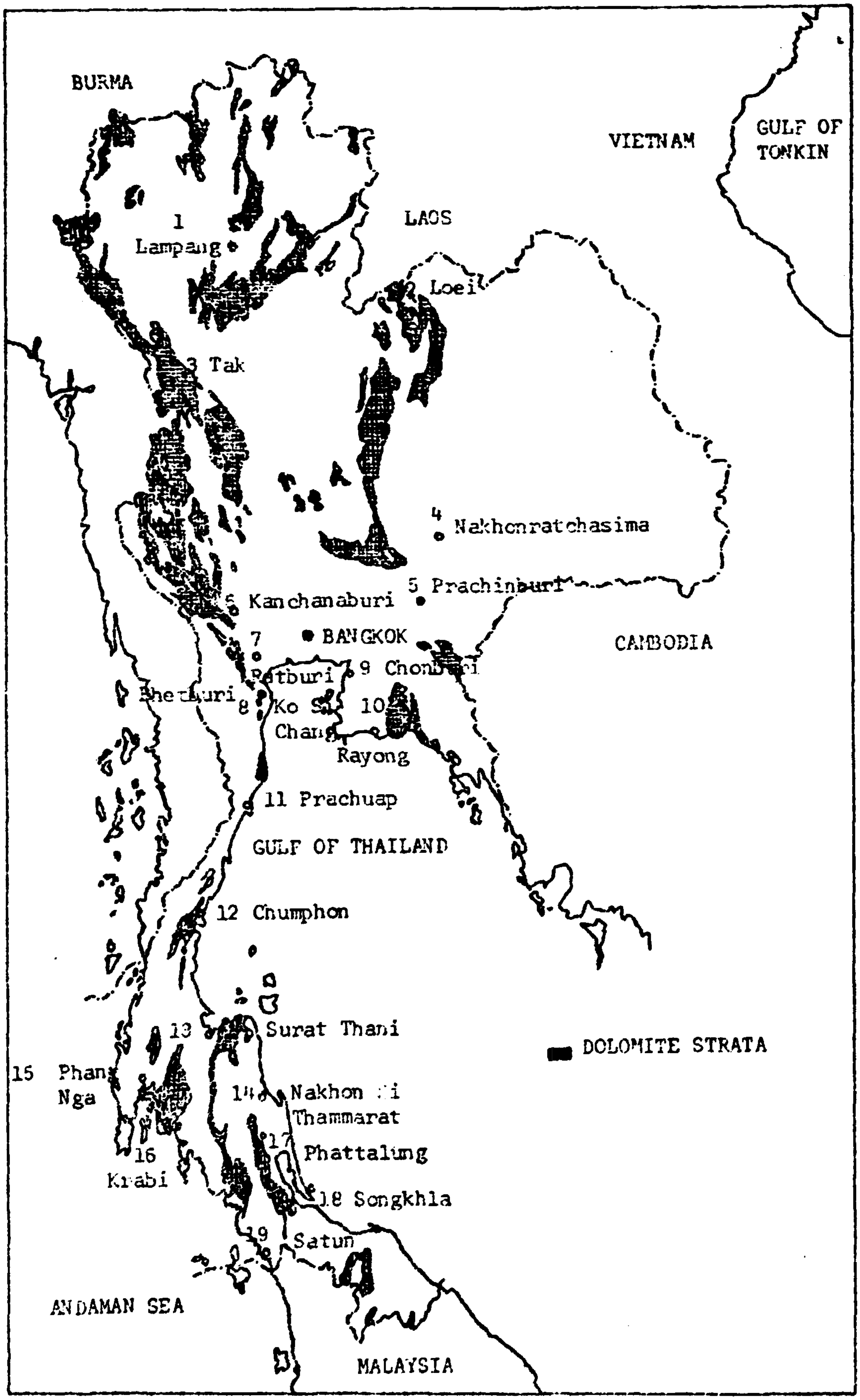


FIG. II.1 DOLOMITE LOCATIONS IN THAILAND

All the evidence points to the "spine" of Thailand being part of a geological fold system and consequential erosion not unlike the Pennine Chain of the U.K. Subsequent evidence revealed that the formations in the centre of Thailand and along the eastern coastal region of the Gulf of Thailand are similar and represent another major fold in the system although not as intense, topographically, as the western complex.

With our limited geological prospecting facilities, the difficulty of the terrain and the major faulting and structural complexity of the region, only a simplified picture can be presented, but the concept of a major anticline explains many of the interesting features of dolomites in Thailand - a point which will emerge later in this chapter.

The age of the anticlinal folding cannot be predicted because there is evidence of unconformity in the depositional cycle. Alexander[5] has suggested that it probably occurred in the late Triassic/early Jurassic era, namely 150-200 x 10^6 years ago because this is the probable age of the under-lying granite. It would be safe to conjecture that it pre-dates the formation of the Himalayas to the north of the country. The northern extremity of the anticline is much more elevated but the exposures are mostly Devonian/Carboniferous; there was also evidence of some E - W folding superimposed on the main anticline. This secondary uplift and folding could be attributed to the massive E - W folding which was responsible for the Himalayan formations.

Fig. II.2 is a simple, generalised representation of the folding followed by weathering erosion pattern which has led to the formation of the Thailand "spine" and to the outcrops of dolomite, throughout the length of the country. It must be stressed, however, that the actual geology is highly complicated because of secondary wave anticlines, a massive fault pattern and later uplift and folding from the Himalayan formation.

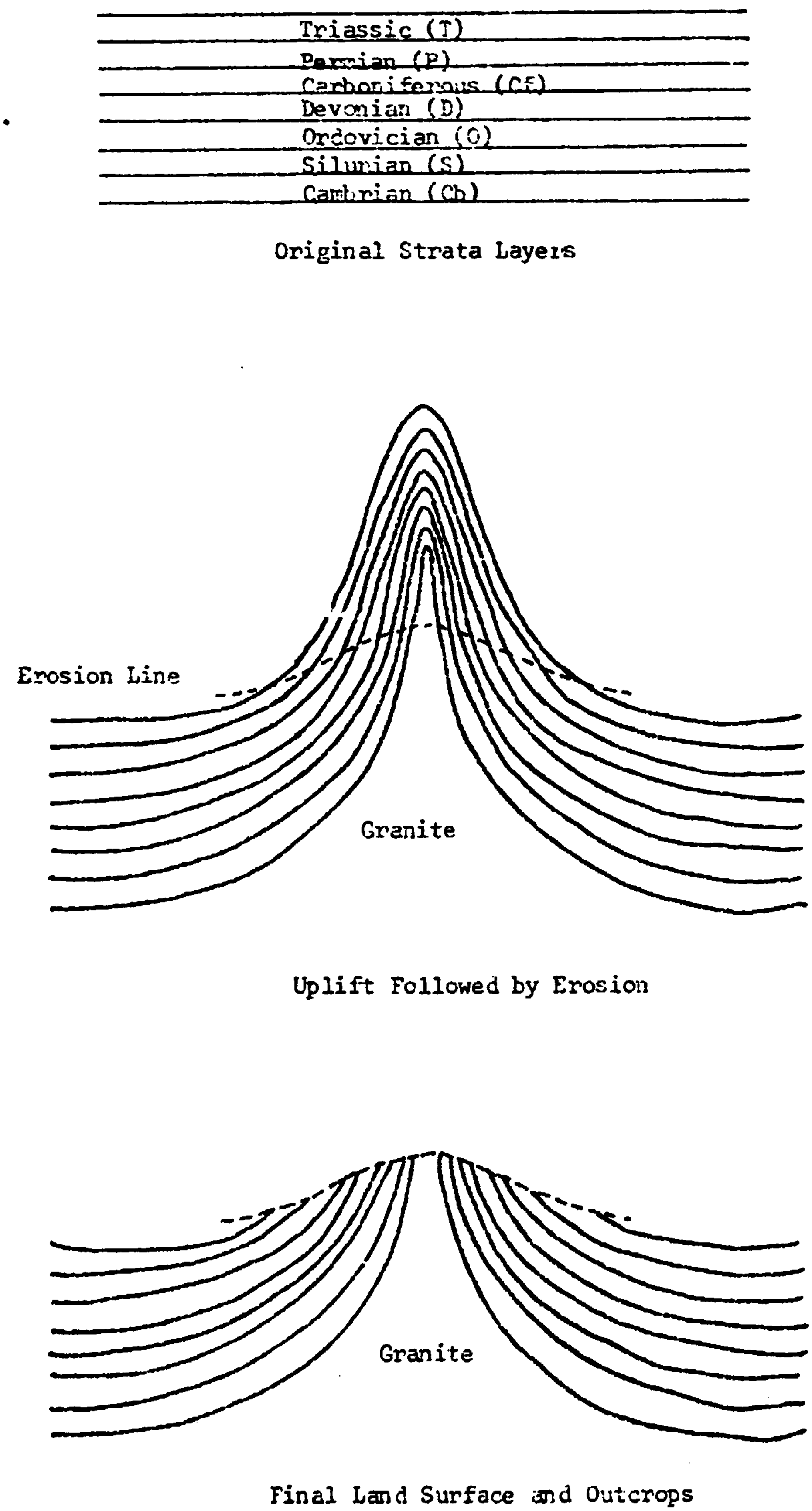


Fig. II.2. Representation of the Geological Formation of the Peninsula of Thailand

Geology of Dolomite in Thailand

It has been known for some time[6] that there were many rock formations in Thailand which were carbonates and which have been generalised as limestones in the literature. Chemical analyses have shown that some of these limestones are dolomite, the mixed calcium/magnesium carbonate.

These formations have not been studied in detail as part of a geological exercise so it is not certain whether all dolomites in Thailand are of the same age. The situation is further complicated because the dolomites are frequently inter-stratified with true lime-stone; they are virtually fossil-free and they are highly pressure metamorphosed.

Buravas[4] has claimed that dolomites occurring around Kanchanaburi (N.W. of Bangkok) are of the Carboniferous era (Kanchana-buri series). Whereas Alexander[5] suggests that formations in the south of the peninsula near to Songkhla and Satun are Permian/Carbonaceous (Ratburi series).

These contentions are difficult to substantiate and our work suggests that the dolomites which we have examined throughout a large area of Thailand are mostly of the same geological age and most probably Carbonaceous/Devonian. No fossils have been found to substantiate this theory but there is some structural evidence.

In the Ratburi area, carbonate rocks are quarried on a large scale for aggregate. These deposits are in the form of low hills which run parallel to the main direction of the anticline. Most of the hills where exposures occur were composed of true white limestone with a bedding which was near to horizontal. In some areas there were other hills with a different contour profile of grey rock and which proved to be dolomite. In the exposures, the dolomite was seen to be highly contorted with a steeply-inclined dip direction. From the fault pattern in the area, it is likely that the dolomite formations were a localised up-lift and that in the normal series they underlie the limestone, which was, almost certainly, of the Ratburi series in that a few fossil graptolites were identified.

In the south of Thailand near to Hat Yai we located a quarry where the lower formations were of grey, contorted, near-vertical rock above which was a whiter formation with a different bedding much nearer to horizontal. The lower levels proved to be dolomite whereas the upper was limestone, which rested unconformably on the dolomite.

Steeply-dipping strata were a feature of dolomites throughout Thailand, but in some localities, particularly near Kanchanaburi and Ko Si Chang there were associated levels of limestone which were of the same geological age. Frequently the limestone and the dolomite were interstratified. In these locations it was extremely difficult to differentiate between dolomite and limestone in the field. Where a quarry was operating some of the senior workmen could tell the difference by observing the fracture plane but neither my supervisors nor I could acquire the technique.

In the initial stages of the survey only analysis in the laboratory could differentiate between the two rocks, but eventually a field test was developed which has proved reasonably successful. This is described in Chapter IV.

In summary, therefore, our work suggests that dolomites in Thailand occur mainly in carbonate rocks of the Kanchanaburi series which is of the Carbonaceous/Devonian era. These underlie, unconformably, other carbonate rocks of the Ratburi series which are Permian/Carbonaceous. No dolomite has been found in this younger series.

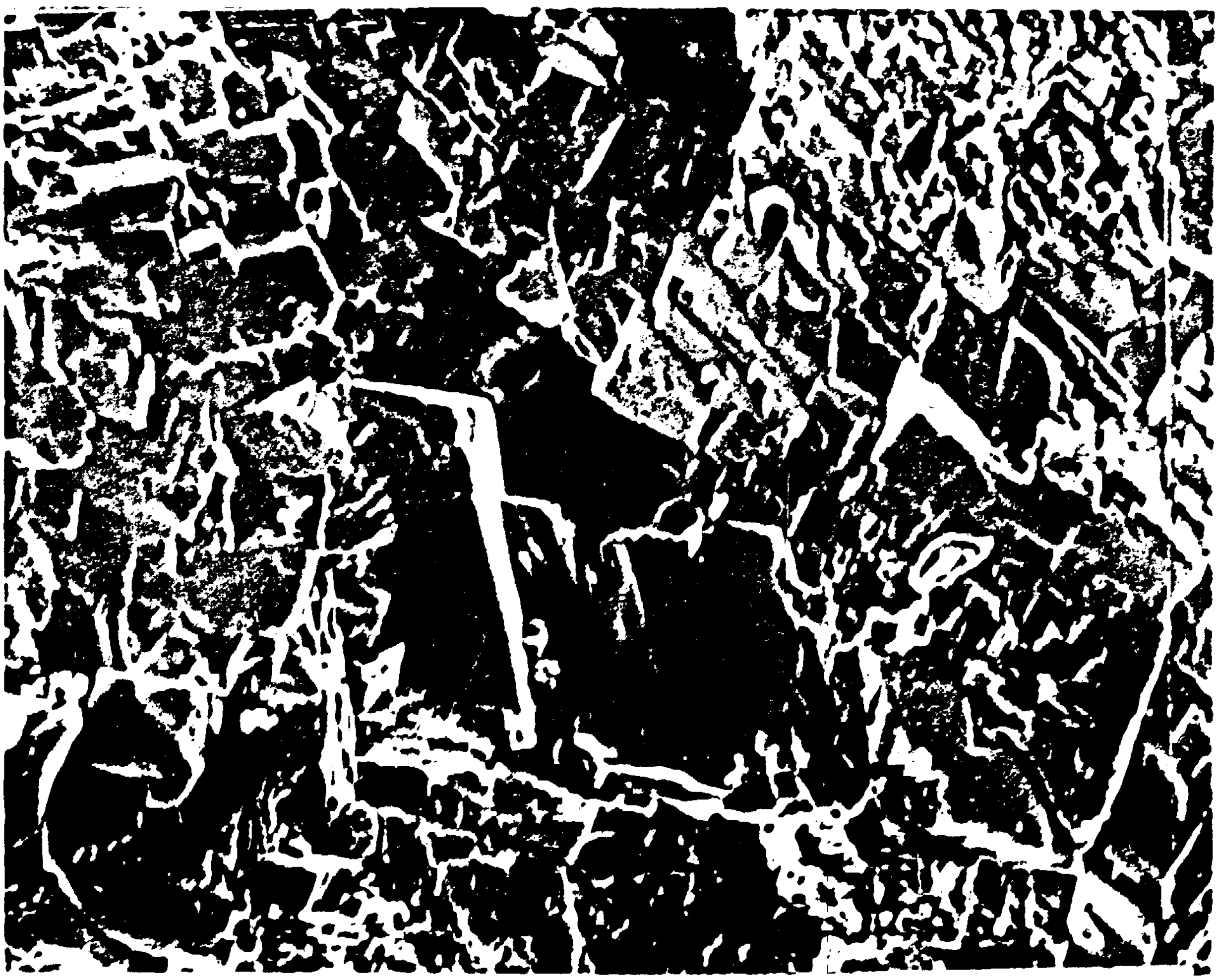
The Nature of Dolomite

Dolomite is a double carbonate of calcium and magnesium but it is a compound rather than a mixture of calcite and magnesite. Dolomite was first recognised as a distinct mineral by the French Geologist, Dolomieu in 1791. The dolomite mountains of the Southern Tyrol where he carried out his pioneer geological work were subsequently named in his honour as was the mineral itself.

The ideal mineral dolomite contains equimolecular amounts of $CaCO_3$ and $MgCO_3$ so that theoretically pure dolomite should contain 45.7% $MgCO_3$ and 54.3% of $CaCO_3$ by weight which is equivalent to CaO 30.4%, MgO 21.7%, CO_2 47.9% (58.3% CaO, 41.7% MgO, on a calcined basis). In the ideal structure [8] Ca^{2+} and Mg^{2+} ions alternate in the lattice but there is probably considerable inter-substitution of the two ions and mostly there is an excess of calcium over magnesium, but this may be due to calcite association. Substitution of Fe^{2+} for Mg is common (Ankerite). Small amounts of Mn^{2+} and Zn^{2+} may substitute for Mg^{2+} and similarly Pb^{2+} for Ca^{2+}.

Crystallography The crystal habit of dolomites is usually rhombohedral[9] but mostly the deposits are massive; a fracture surface will frequently show the rhombohedral form under the Scanning Electron Microscope (Fig. II.3). Crystals of other forms are rare but not unknown. Deposits range from coarse, granular, cleavable masses to fine-grained and compact varieties with others vitreous and pearly. Twinning on

a. Wülfrath, Germany Dolomite



b. Kanchanaburi Dolomite

Fig. II.3 - Scanning Electron Micrographs of Raw Dolomites

0001 is common, also lamellar twinning on 0221. Hardness is between 3½ to 4 on Moh's scale and specific gravity is about 2.85. The colour is usually some shade of white, grey, brown, yellowish or black depending on impurities. Dolomite is slowly soluble in dilute HCl, but it may be distinguished from limestone by its less vigorous reaction with the acid.

Major Occurrences. Dolomite is found in many parts of the world chiefly as extensive sedimentary strata. Dolomite, as a rock mass, is now considered by most experts to be secondary in origin[10], formed from limestone by the replacement of calcium by magnesium in percolating water. The replacement may be only partial and thus most formations are mixtures of dolomite and calcite. The mineral occurs also as a hydrothermal vein mineral. The theory that it may precipitate directly from sea water is no longer tenable[11].

Natural occurrences usually contain impurities, the main ones being SiO_2, Fe_2O_3 and Al_2O_3 present mostly as sedimentary minerals e.g. clays, quartz. For dolomite to be used as a refractory it must be low in these impurities. Other contaminants such as compounds of boron, phosphorus and vanadium must not be present in greater than trace quantities. In general dolomite for refractory grades should contain not less than 18% MgO with the maximum amount of impurity not to exceed 4% and preferably less than 2.5%. SiO_2 should not be more than 0.8%, Al_2O_3 not more than 1.5% and Fe_2O_3 also not more than 1.5%[12]. Dolomite for the sea water magnesia process must be of purer quality and manufacturers are nowadays looking for less than 1.0% total impurity[13] but such deposits are very rare.

Dolomites for use as refractories need to possess other important properties over and above chemical purity. They must calcine readily, and at high temperatures (+1600°C) they must sinter to a mass of low porosity. Commercial deposits must be massive and uniform in quality. Above all they must be easily mined, need little or no mineral benefici-ation and they must be low-priced when delivered to the user.

It was these considerations which governed the scope of the present survey. There are known deposits of dolomite in north-west Thailand but because of the centralisation of industry in the areas near to Bangkok, it would be impractical (because of transport problems) and uneconomical (because of cost of transport) to give consideration to deposits north of Kanchanaburi. However, because of the close proximity of the sea, all dolomite occurrences in the peninsula and near to the east coastline of the Gulf of Thailand might be of value for a sea water magnesia plant.

The preliminary survey was, therefore, conducted on the basis of samples analysed as dolomite by D.M.R., reports from several other sources and our own geological inspection particularly in areas where industrial development might be viable.

Dolomite in Thailand

Fig. II.1 is a map of Thailand showing from geological data (not necessarily accurate) probable areas in which dolomitic strata might outcrop. It was in these areas that superficial surveys were carried out to collect the initial samples. At the same time, a search of D.M.R. records enabled further locations to be established. These dolomite occurrences are identified on the map and their analyses are shown in Table II.I.

TABLE II.1. CHEMICAL ANALYSES OF THAILAND DOLOMITES

Location	Chemical Analysis %					
	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	LOI
1. Lampang	16.2	32.1	4.07	1.36	0.45	-
2. Loei	19.2	30.6	2.14	0.54	0.40	-
3. Tak-Mae Sot	19.8	31.2	0.23	0.30	0.92	45.6
4. Nakhonratchasima	18.2	34.8	0.10	-	0.18	-
5. Prachinburi	17.8	30.5	-	-	-	-
6. Kanchanaburi						
6.1. Khao Wang	18.7	32.8	0.39	0.66	0.60	-
6.2. Khao Poon	18.4	32.8	0.36	0.34	0.13	-
6.3. Khao Ban Thum	21.4	29.6	1.80	0.18	0.35	-
6.4. Khao Ban Rai	20.7	31.7	0.03	0.00	0.24	47.4
6.5. Ban Wang Dang	20.9	30.6	-	-	0.60	-
6.6. Huai Mang Lak	19.7	32.3	-	-	-	-
6.7. Ko Sam Rong	19.3	34.7	0.04	0.35	0.33	-
6.8. Khao Rad	18.6	33.8	0.23	0.00	0.25	-
6.9. Khao Phu Lom	20.7	31.0	0.84	0.02	0.03	47.0
6.10. Khao Laem	19.5	31.5	0.40	0.03	0.07	47.0
6.11. Ban Chao Nen	19.1	32.5	0.96	0.00	0.28	47.2
7. Ratburi						
7.1. Khao Klang Noen	20.2	32.4	0.26	0.47	0.19	46.7
7.2. Khao Nom Nue	19.4	31.4	0.08	0.40	0.33	46.3
7.3. Khao Lom Rue	16.4	35.2	0.84	0.28	0.44	45.9
7.4. Khao Kak	21.6	31.2	0.23	0.35	0.15	46.5
7.5. Khao Ngu	0.2	54.4	0.48	0.59	0.28	43.1
7.6. Khao Lak Waw	21.2	31.8	0.01	0.01	0.46	46.7
7.7. Khao Pra Than Chang	19.4	32.7	0.41	0.34	0.56	45.8
8. Phetburi						
8.1. Khao Yoi	21.0	31.5	0.08	0.14	0.14	46.5
8.2. Khao Bandi It.	21.3	31.2	0.18	0.12	0.15	46.8
9. Chonburi						
9.1. Bang Pra	17.9	33.6	3.41	1.58	0.62	43.4
9.2. Ko Si Chang	16.3	34.0	4.17	2.11	0.48	43.1
9.3. Ko Khang Khao	17.4	33.2	2.05	0.67	0.47	45.3
9.4. Khao Choeng Tean	20.6	31.8	3.32	1.60	0.72	42.5

Cont.

Table II.I Continued

Location	Chemical Analysis %					
	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	LOI
10. Rayong						
10.1. Klaeng	20.1	30.8	0.96	0.66	0.45	46.0
10.2. Klang Tung	18.1	34.8	0.02	0.14	0.36	-
11. Prachuap(Khiri Khan)						
11.1. KM 378/9	18.8	32.9	0.04	0.00	1.4	44.5
11.2. Pranburi	21.6	30.9	-	-	-	-
11.3. Bangsapan Yai	22.2	31.3	-	-	-	-
11.4. Hua Hin	20.3	32.6	0.04	0.38	0.67	45.9
12. Chumphon						
12.1. La Mae	19.9	33.4	0.17	-	0.34	46.7
12.2. Pha To	21.3	30.5	0.23	0.17	0.41	47.2
13. Surat Thani						
13.1. Kirirat Nikom	20.9	31.7	-	-	-	-
13.2. Kuan Sak	20.6	31.9	0.13	0.00	0.50	46.9
13.3. Chai Ya	20.3	31.6	0.31	0.26	0.62	46.7
13.4. Khao Bo Nam Ron	21.2	30.3	0.25	0.11	0.49	47.3
13.5. 17P/BB1	15.2	35.4	1.64	0.06	0.70	44.7
13.6. Kanchanadit	19.1	32.9	0.18	0.00	0.69	46.5
13.7. Plai Mas	21.3	29.8	0.81	0.35	0.40	46.8
13.8. Tha Chana	18.2	34.7	0.17	0.00	1.54	45.2
13.9. Khao Noi	21.2	31.3	0.11	0.32	0.01	47.2
14. Nakhon Si Thammarat						
14.1. Khao Hua Chang	17.7	35.4	0.11	0.00	0.46	46.1
14.2. Khao Wang	18.9	33.5	0.64	0.13	0.61	45.9
14.3. Cha Uat	21.0	30.9	0.21	0.18	0.20	47.0
14.4. Khao Koi	21.1	31.1	0.22	0.24	0.31	46.8
15. Phang Nga	18.0	34.5	1.14	0.07	0.56	45.7
16. Krabi	20.5	32.2	0.17	0.11	0.30	-
17. Phatthalung	20.3	29.7	2.99	-	0.95	44.1
18. Songkhla						
18.1. Khao Rung	20.9	31.8	0.00	0.00	0.27	46.6
18.2. KM 28	17.6	32.0	4.88	1.18	0.73	44.4
19. Satun	7.2	37.5	6.25	0.99	0.83	38.6

Unfortunately not all reports of dolomite were substantiated and there were several areas which could not be visited because of military restrictions but some promising deposits were located. Some of these were small working quarries usually for aggregate and in these places extensive sampling was possible.

Detailed Occurrences of Dolomite

The preliminary survey established that dolomite formations were to be found in many parts of Thailand and that they were probably of similar geological origin and age. It is likely that deposits outcrop at many places on the eastern side of the Thailand peninsula and also along the east coast of the Gulf of Thailand. Whether all or any of the deposits could be of value industrially remains to be proved because, in addition to chemical purity, deposits must be of sufficient size, uniform in quality and accessible for development.

For these reasons several dolomite locations were examined and sampled in detail.

Five principal areas were selected as follows:-

6. Kanchanaburi 7. Ratburi (both West of Bangkok).

9. Ko Si Chang an island offshore the east coast of the Gulf of Thailand.

18. Songkhla 19. Satun (both in the extreme south of the peninsula with the former being on the east and the latter on the west coast).

In addition, areas near Phetburi and Chumphon should have been examined in detail but the reported dolomite exposures, were inaccessible and in areas subject to military control. These should be sampled at a later date.

In all the areas selected, the dolomites occurred as exposures along the face of a hill or range of hills so that the mineral could be identified and sampled over a considerable extent.

Kanchanaburi. There were several promising locations of potential dolomite in the Kanchanaburi area. The positions of these deposits are shown in the map (Fig. II.4). All of these were quarries, some of which were still being worked, mostly for aggregate and some for burnt lime or fluxes.

In seven cases, a complete face was sampled both horizontally and vertically usually at 10 or 20 mts. intervals. The analyses of material from all these collection points are shown in Table II.II.

Materials from KMN and KS were the most promising in terms of dolomite quality, consistency and in total volume and these were selected for further work in the research programme.

KMN was a quarry along the east bank of the river Khwae Noi. It was part of a small range of hills known as Khao Laem which extends for about 25 Km along the river. The exposure KMN was 120 mt long and 40 mt. high but the hill attained a height of about 120 mt and it extended about 3 Km in an easterly direction. Dolomite was found at locations over the complete hill range. With confidence, it can be predicted that over 500,000 tonnes of good quality dolomite would be present in the KMN area but there could be over 2×10^6 tonnes.

KJ was a smaller quarry to the west of KMN. Much of it was dolomite of good quality but there was an interstratified band of calcite which reduced the average MgO content.

KS was a massive quarrying complex (by Thailand standards) again in the Khao Laem range and owned by the Suthasahathai Company. There were six exposed faces all of which were sampled systematically. The extracted stone was being used mainly for aggregate and as a flux

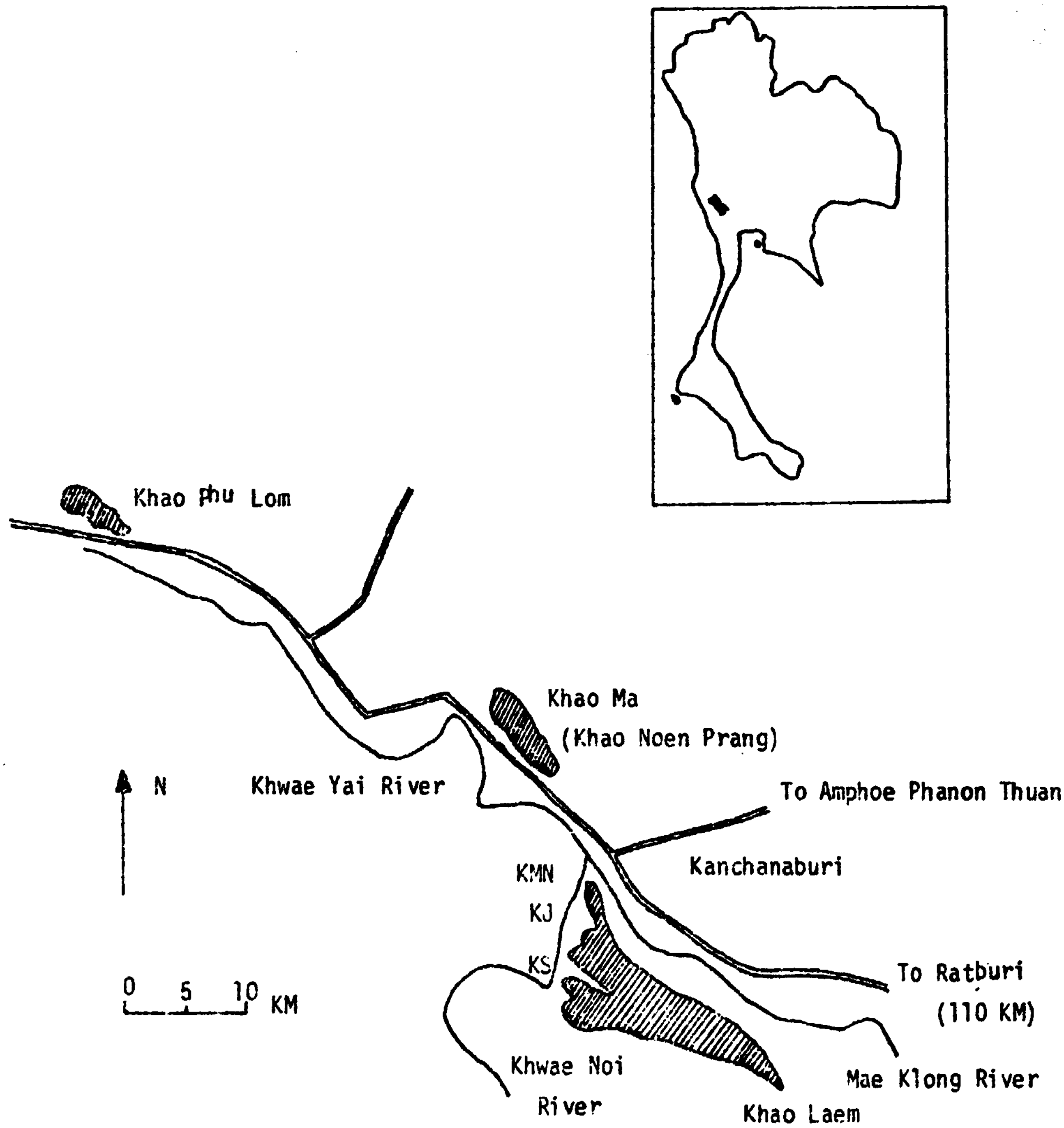


FIG. II. 4 : DOLOMITE DEPOSITS IN KANCHANABURI AREA

TABLE II.11 - ANALYSES OF DOLOMITE OCCURRENCES IN KANCHANABURI AREA

Location	Number of Samples	Chemical Analysis, %									
		MgO			CaO			SiO_2	Al_2O_3	Fe_2O_3	LOI
		high	low	median	high	low	median	(ave)	(ave)	(ave)	(ave)
Kanchanaburi Area											
Khao Phu Lom	36	22.0	10.2	20.9	40.9	30.3	32.0	0.85	0.02	0.07	45.9
Khao Ma	7	16.2	0.7	4.4	52.7	34.5	47.9	2.85	0.21	0.83	43.4
Khao Laem KS											
Face 1	19	21.4	19.1	20.1	32.9	30.0	31.3	0.38	0.02	0.03	47.1
Face 2	32	20.6	6.1	18.8	47.2	31.2	35.7	0.31	0.02	0.05	46.6
Face 3	12	21.0	20.4	20.7	31.5	30.7	31.1	0.22	0.02	0.02	47.3
Face 4	9	20.8	3.5	16.1	50.3	31.2	35.6	0.34	0.02	0.03	46.6
Face 5	26	20.9	0.6	17.6	54.2	31.0	37.0	0.28	0.01	0.05	46.9
Face 6	14	20.7	1.5	12.5	54.0	30.8	41.3	0.31	0.02	0.05	46.4
Khao Laem KJ	10	19.9	0.6	13.0	53.4	30.2	39.1	0.13	0.10	0.07	45.4
Khao Laem KMN	28	21.4	19.9	20.8	32.0	29.8	30.7	0.15	0.02	0.03	48.0

for the steel industry. The limestone faces were being burnt for agricultural lime.

Three faces of the KS quarry complex showed good and consistent dolomite and from geological and topological observation it would be safe to predict that at least 1.5×10^6 tonnes of dolomite could be extracted.

Khao Ma was a quarry in a hill on the north bank of the river (in the area called Khwae Yai which has been anglicised to Kwai). It appeared to contain dolomite but the quantity of high MgO material was small.

Khao Phu Lom, the most northerly formation examined, was different in appearance from other dolomite formations but it proved to be of consistently good quality. A large face - about 40 mt. high and 200 mt. lateral extent - was exposed. The entire hill which was sampled over its whole extent was good quality dolomite and could contain over 3×10^6 tonnes of mineral. Subsequent tests showed that in parts of the deposit there was talc (hydrate magnesium silicate) associated with the dolomite.

The samples from the best faces of KS and from the whole exposure of KMN were each separately compounded and representative samples of about 80 Kg sent to the U.K. for research purposes.

Ratburi. There were reports of working quarries of limestone in the Ratburi area, and the records showed some locations containing high quality dolomite and many others with a lower MgO content. Ten locations were sampled as shown in Fig. II.5 with chemical analyses included in Table II.III.

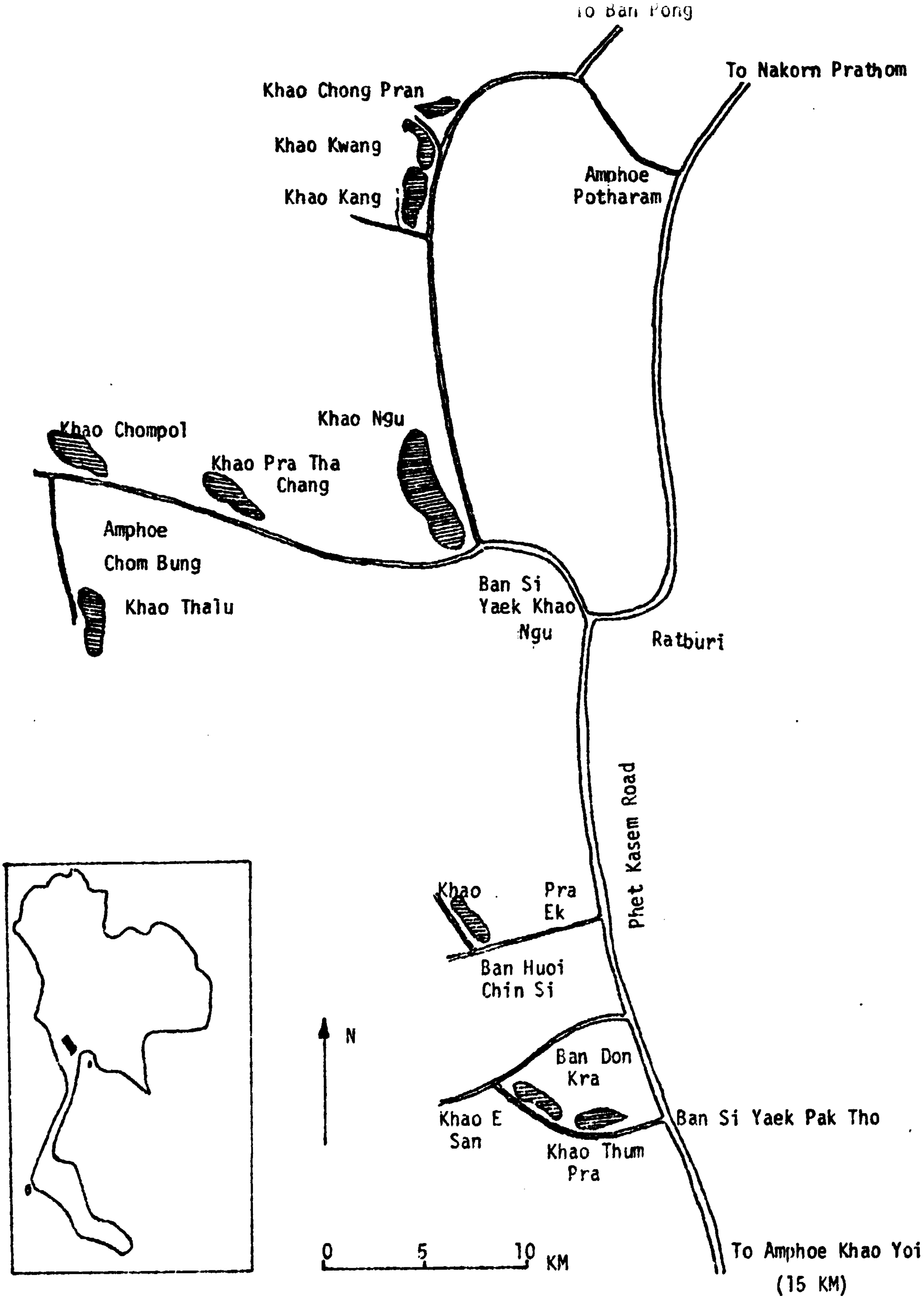


FIG. II.5. : DOLOMITE DEPOSITS RATBURI AREA

TABLE II.III. ANALYSES OF DOLOMITE OCCURRENCES IN RATBURI AREA

	Number of Samples	Chemical Analysis % MgO high	MgO low	MgO median	CaO high	CaO low	CaO median	SiO_2 (ave)	Al_2O_3 (ave)	Fe_2O_3 (ave)	LOI (ave)
Ratburi Area											
Khao Ngu	6	1.2	0.3	0.4	54.2	53.2	54.0	0.68	0.31	0.42	44.0
Khao Kang	21	21.1	1.1	20.0	54.3	30.8	32.0	0.26	0.02	0.23	47.2
Khao Kwang	22	21.8	16.5	21.4	36.0	30.2	30.6	0.08	0.02	0.22	47.5
Khao Chong Pran	11	20.1	0.3	0.7	54.2	31.1	43.5	0.80	0.04	0.28	44.0
Khao Thalu	2	0.6	0.6	0.6	54.1	54.0	54.0	0.80	0.04	0.28	44.0
Khao Thum Pra	2	0.6	0.5	0.5	55.5	54.7	55.1	0.25	0.06	0.06	43.8
Khao E San	2	0.9	0.5	0.7	54.9	53.5	54.2	0.84	0.36	0.06	43.8
Khao Pra Ek	1			0.6			52.3	4.12	0.67	0.07	42.3
Khao Chompol	2	0.6	0.6	0.6	53.0	53.0	53.0	2.38	0.35	0.14	42.9
Khao Pra Thap Chang	2	18.5	10.9	14.7	32.8	30.5	31.6	5.56	0.08	0.20	43.5

Khao Ngu was the largest quarry in the area of massive grey limestone; there were several exposed working faces and a crushing plant for road stone. Samples were collected at random and they were all of limestone. This was a different stone from the dolomite exposures and it is probably Carbonaceous/Permian i.e. younger than the dolomite formations.

Khao Kang was a hill about 50 metres high and 150 metres long. There was no quarrying but samples were collected systematically from north to south which were all grey dolomite of contorted vertical strata except for a white interstratified rock in one area which was like marble and contained virtually no MgO.

Khao Kwang was a hill about 4 Km north of Khao Kang; it was about 80 metres high, 400 metres long and 200 metres wide; the rock was exposed over all the area. It was extensively sampled both vertically and horizontally, and all samples proved to be good dolomite. There could be over 20×10^6 tonnes of useful material in this area, but systematic drilling would be required to prove this assertion.

Khao Chong Pran was another hill about 3 Km further along the road; there was a similar type of rock exposure but there proved to be much more interstratified limestone in this formation.

Six areas south and west of Ratburi were sampled, most of which had a low MgO content (See Table II.III) and for the most part they were of the Carboniferous/Permian strata found in Khao Ngu quarry.

Khao Kwang was selected as the best material in this area and a large quantity was sampled for shipment.

<u>Ko Si Chang and Ko Khang Khao</u>. These two islands off the east coast of the Gulf of Thailand were both sampled systematically with more than 200 samples taken for chemical analysis. (Fig. II.6. and Table II.IV). Most of the dolomite deposits were found at Laem Ngu, Laem Si Chang and area I of Ko Khang Khao of which the

first was the most significant. This was bulk sampled.

Songkhla and Satun Area. Five locations were sampled from this areas as shown in Fig.II. 7 and chemical analysis in Table II.V.

Khao Rak Kaet was a quarry in a small hill which supplied a product for road stone. Samples were taken at 10 metre intervals from north to south; the quarry face was about 80 x 400 mts. Two caves in the limestone were found, one of which contained phosphates from bat-droppings and was being worked on a small scale. This was an interesting exposure in that the dolomitewas a highly contorted grey rock underlaying a more horizontally bedded true limestone probably of different geological ages.

Khao Khuha, had many quarries working for aggregate, with an associated large crushing and grinding plant. Samples were all low in MgO and the material was a true limestone.

Khao Changlon was a similar rock formation to Khao Khuha.

Khao Nui had a small quarry exposure which looked like dolomite but which proved to be limestone. There was an infilled cave with well developed calcite crystals.

Khuan Lek was a hill along the side of the road about 30 Km from Satun but in the western coastal strip. It was a massive hill but it was difficult to sample systematically because of the thick vegetation and steep contours. Twenty three samples were collected along a level near to the road over the 400 mt. of exposure. Most were dolomite.

The visit to the Songkhla/Satun areas involved considerable travelling. The deposits of dolomite were rich in magnesia but the impurity levels (particularly silica) were much higher than those from deposits further north. Rather than collecting a bulk sample from one location which would have required an additional visit, materials from

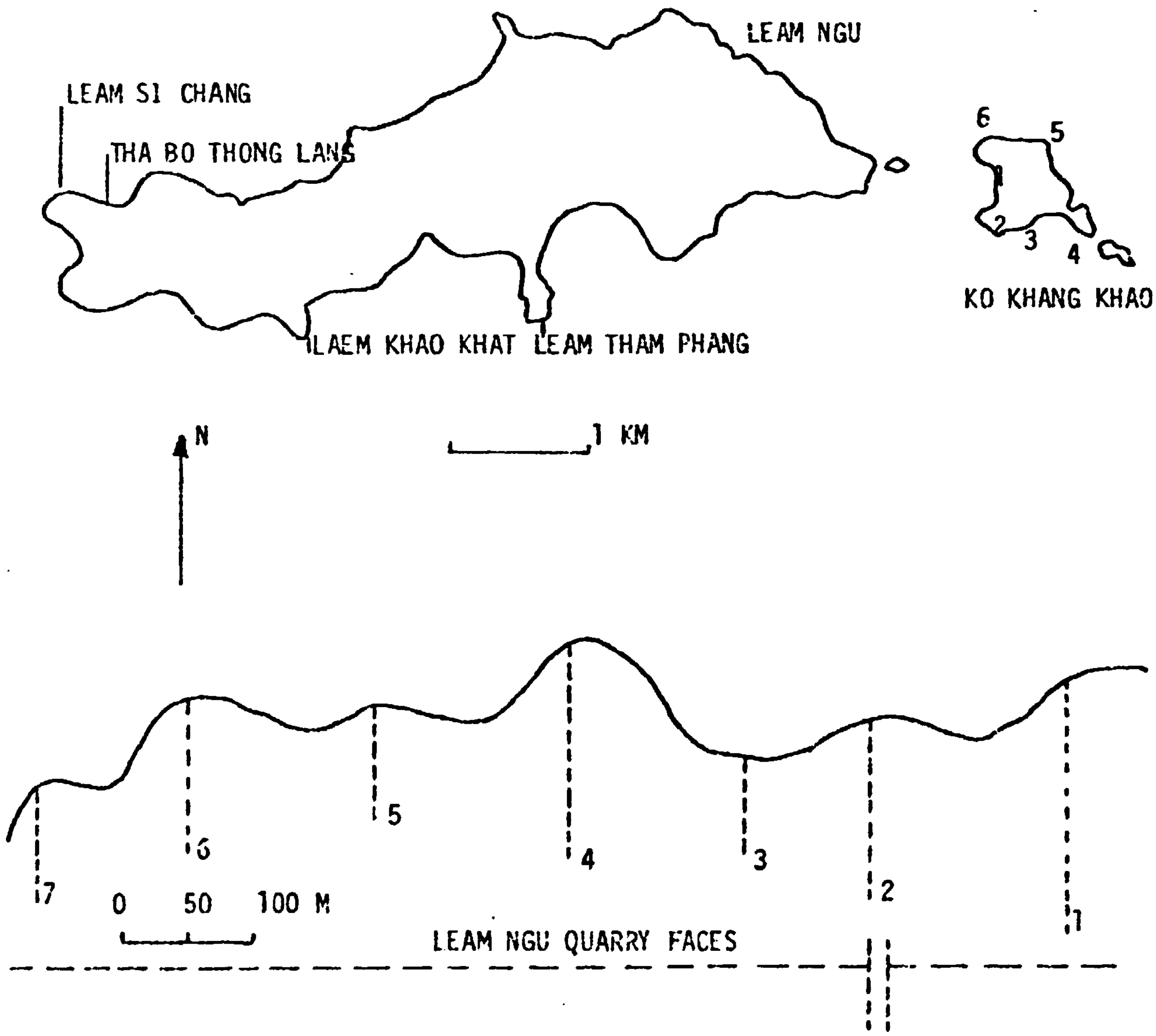


FIG. II.6 - KO SI CHANG AREA OF DOLOMITE EXPOSURE

TABLE II.IV. ANALYSES OF DOLOMITE OCCURRENCES IN KO SI CHANG AREA

Location	Number of Samples	Chemical Analysis, %									
		MgO			CaO			SiO_2	Al_2O_3	Fe_2O_3	LOI
		high	low	median	high	low	median	(ave)	(ave)	(ave)	(ave)
Ko Si Chang Area											
Laem Ngu											
Face 1	26	18.8	3.4	15.9	44.3	30.3	33.4	3.87	1.04	1.22	42.9
Face 2	12	17.9	14.8	17.0	32.6	31.3	32.1	6.30	1.24	0.80	41.1
Face 3	12	19.2	14.0	17.2	32.6	30.4	32.4	4.54	0.87	0.72	44.3
Face 4	24	19.6	1.1	8.1	52.0	30.0	39.9	8.72	0.89	1.04	39.0
Face 5	8	0.8	0.2	0.6	35.2	28.2	30.0	25.82	8.0	1.41	24.0
Face 6	11	3.1	0.7	2.1	55.2	27.6	46.5	8.15	0.55	1.07	40.2
Face 7	7	2.0	1.0	1.2	43.5	33.1	40.1	6.78	1.22	0.44	40.4
Laem Khao Khat	4	1.2	0.6	0.7	30.1	17.4	19.6	47.74	11.99	1.95	8.95
Laem Si Chang	10	19.5	6.6	16.6	44.2	33.5	35.7	4.03	0.60	0.86	45.3
Tha Bo Thong Lang	6	19.7	16.4	17.4	34.6	33.2	33.4	2.05	0.67	0.47	45.3
Laem Tham Pang	3	0.3	0.0	0.1	12.0	10.5	10.9	76.07	1.12	0.21	10.5
Ko Khang Khao											
Area 1	32	16.6	0.2	8.9	50.2	32.0	40.1	5.79	0.92	0.72	43.1
Area 2	15	19.2	15.1	12.4	34.6	33.4	33.6	2.48	0.60	0.84	42.7
Area 3	12	8.5	0.9	2.6	46.7	37.4	43.3	9.01	4.04	1.04	34.1
Area 4	22	2.7	0.2	0.8	50.2	40.9	44.0	9.22	1.12	0.32	40.0
Area 5	18	4.3	0.9	0.9	49.0	42.9	43.8	18.60	0.60	0.72	35.6
Area 6	18	2.5	0.4	2.1	49.7	43.8	48.2	9.21	0.94	0.90	40.0

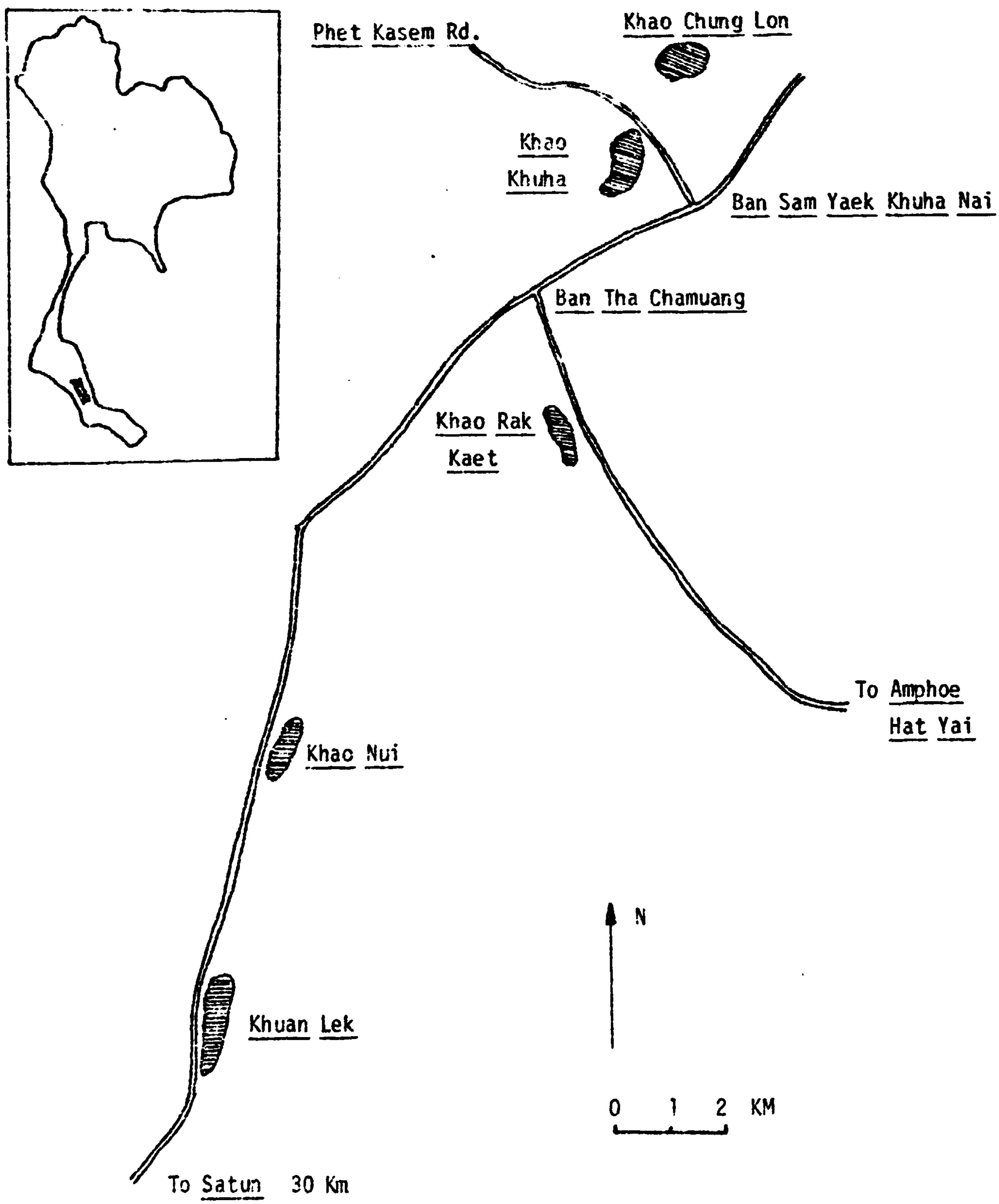


FIG.II. 7 : DOLOMITE DEPOSITS IN SONGKHLA/SATUN AREAS.

TABLE II.V . ANALYSES OF DOLOMITE OCCURRENCES IN SONGKHLA AND SATUN AREAS

Location	Number of Samples	Chemical Analysis, %									
		MgO			CaO			SiO_2	Al_2O_3	Fe_2O_3	LOI
		high	low	median	high	low	median	(ave)	(ave)	(ave)	(ave)
Songkhla and Satun Areas											
Khao Rak Kaet	16	19.9	0.9	17.2	54.2	29.9	32.1	6.58	0.88	1.20	42.5
Khao Khuha	3	2.2	0.3	0.6	54.2	44.4	46.9	3.83	0.83	0.09	41.5
Khao Chang Lon	2	0.7	0.7	0.7	44.9	42.9	43.9	9.18	1.83	1.28	39.4
Khao Nui	5	2.3	0.7	1.7	51.7	42.9	50.9	4.83	1.20	1.04	40.9
Kuan Lek	23	19.4	0.9	16.2	49.2	31.5	33.0	6.94	0.70	0.92	42.1

Khao Rak Kaet and Khuan Lek were mixed together to provide a bulk sample typical of southern Thailand dolomites.

General Observations on Thailand Dolomites.

Several interesting observations and conclusions can be drawn from the survey of Thailand dolomites.

1. There are many deposits in the country and surface formations are to be found in many areas which would be convenient for exploitation by simple quarrying.
2. There is a wide range of qualities throughout the country. Many deposits were close to the theoretical maximum ratio of MgO:CaO contents. Within this classification, deposits ranged from those of very low impurity levels ($SiO_2 + Al_2O_3 + Fe_2O_3$) of less than 0.5% to those where in excess of 6% was present. It should be possible to find suitable deposits to match any required specification.
3. Several deposits which were examined in detail should contain over 1×10^6 tonnes of consistent material.
4. In most Thailand dolomites, the iron oxide content was low when compared with other world sources. This is probably an advantage.
5. One of the most significant features when surveying the analyses of the dolomites which occurred from north to south in the western anticline was the variation in impurity content - particularly the silica.

Near to Kanchanaburi in the north, silica levels were consistently low at 0.1 - 0.2% whereas in the Songkhla/Satun southern area the silica was high - frequently above 6%. showing the north - south trend.

Table II.VI taken from the information in earlier tables illustrates this point.

Table II.VI. Silica Content of some Thailand Dolomites

Area	SiO_2 Content %
Kanchanaburi	0.15
Ratburi	0.25
Phetburi	0.18
Prachuap Khiri Khan	0.04
Chumphon	0.21
Suratthani	0.35
Pang Nga	1.1
Nakhon Si Thammarat.	0.8
Phatthalung	3.0
Songkhla	6.5
Satun	6.9

Inspection of the various deposits shows that the major portion of the impurities present in dolomites is in the form of pegmatic veinlets which have arisen from volcanic activity - probably hydrothermal intrusions.

The nearer the dolomite deposit to one of the igneous granitic masses which outcrop along the "spine" of Thailand, the more likely it is that it will be contaminated with pegmatic silica impurity. (See Fig. II.1).

In the Kanchanaburi/Ratburi area, the nearest granite intrusion is about 50 Km, whereas in the Songkhla/Satun area, the granite is only 5 - 10 Km away from the dolomite.

All evidence points to the fact that the anticlinal fold was much more intense in the south of the Thailand peninsula than it was in the north and therefore hydrothermal activity has been much more prominent with the consequent higher level of impurity in southern dolomites.

CHAPTER III

EUROPEAN AND WORLD RESOURCES AND UTILISATION OF DOLOMITE

Until the advent of basic steel-making the only commercial uses for dolomite were as an aggregate, as a flux in glass-making and as a fertiliser.

In the early days of basic open-hearth furnace practice, dolomite had only a limited use because of the technological difficulties of stabilising the mineral for use as a refractory. From about 1936, its value as a precipitant of magnesia from sea water was recognised but the lime component was a deterrent to using the mineral as a refractory in its own right.

In recent years, the importance of dolomite has increased substantially. It is a relatively cheap raw material and its high temperature properties are excellent. By various devices the tendency of the fired product to rehydrate has been minimised. Many more applications have been found for dolomite-based refractories particularly in the modern oxygen steel-making processes.

Much of the technology of dolomite utilisation is a closely guarded secret by the major manufacturers and only ore bodies with specific properties are of value. For these reasons an important aspect of the present research was to survey the dolomite market and to visit manufacturing units and users to assess whether material found in Thailand could be of value in local industries.

World Production of Dolomite

Although it is of widespread occurrence and produced commercially on a large scale (world production probably exceeds 100×10^6 tonnes/year), dolomite is not always recognised as a mineral in its own right. Dolomite is closely related to limestone in its formation, occurrences and even commercial usage. For many purposes the fact that, chemically, dolomite and limestone are different is of little significance and in many countries official records do not differentiate between them. The building, construction and aggregate industries are the major tonnage users of dolomite but they are not interested in the chemical features of the mineral, only the fact that it is hard and durable.

The main industrial uses of dolomite may be classified as follows:-

1. Construction, aggregates etc. which is the largest tonnage use but where chemical quality is of no importance compared with hardness, cheapness and the location of the deposits which must be close to the area in which it is used.

2. Fertilisers, mainly to control acidity of soils. Normally true limestone is preferred for this application; it is burned to remove carbon dioxide and then usually slaked to produce agricultural lime. When dolomite is used, the magnesia content may be troublesome in that $Mg(OH)_2$ is insoluble so the material is less reactive. However, for some horticultural purposes including tea, rubber, sugar beet, magnesium is essential for plant growth and, in these cases, dolomite is of value.

3. Glass-making, where dolomite is an important flux. Careful selection of the mineral is important for this industry; the essential requirement is a low iron-content preferably below 0.2% Fe_2O_3 but users also usually stipulate MgO in excess of 15%.

4. Fillers, extenders for pigments, plastics etc. The chemical quality of the dolomite is of little importance in these applications; a good white colour, hence low iron and carbonaceous material, is of prime importance. Dolomite frequently is preferred to limestone because it is less reactive to mineral acids. In recent years, dolomite has been increasingly used as a potential fire retarder in plastic compositions. Its initial temperature of decomposition is lower than that of limestone and it liberates carbon dioxide over a wider temperature range.

5. Flux in steel-making. The presence of the two alkaline earth oxides, lime and magnesia is of value in controlling the viscosity of slags in steel vessels. Hence dolomites, particular those low in silica, have become increasingly used for this purpose, especially for fast converter processes.

6. Precipitant of magnesia from sea water. Dolomite has the advantage of providing additional magnesia to the process and hence is usually preferred to limestone. However, in recent years, the trend in magnesia production from sea water has been towards purer qualities which demand high purity precipitants. Few dolomite deposits can meet the rigid low content of impurities now being specified - total SiO_2, Al_2O_3, Fe_2O_3 not to exceed 0.4% - and some manufacturers are reverting to limestones. About three tonnes of raw dolomite are required to produce one tonne of magnesia.

7. Refractory uses. New technology coupled with the fact that dolomite is a cheap raw material but with excellent refractory qualities, has led to substantial increases in its use either in brick or block form or as a monolithic.

When calcined at high temperatures, the lime component cannot be stabilised by heat alone and it will rehydrate. A stabilised form of dolomite refractory was produced in which talc or a similar silicate was added to form a calcium silicate but this was not an outstanding success. In modern practice, the dolomite is firstly calcined to a high temperature to sinter fully the oxide components. Careful crushing and grading coupled with high pressure-forming produces a dense compact which can then be given more stability either by bonding with pitch or tar or by ceramic bonding which involves an additional firing. A recently introduced technique involves low temperature firing (circa 1200^{o}C) which gives a highly active oxide mixture, followed by fine grinding and then briquetting. The compact is then refired at very high temperatures to ensure densification and stability. From the resulting product excellent refractories can be produced and this technique is particularly applicable to dolomites of high purity.

Dolomite refractories are now being used in many steel plant applications where rehydration problems can be avoided. These include linings for various new steel converters, ladles etc. Dolomite bricks are also being used for lining cement kilns.

In countries with a highly developed refractory technology coupled with available good raw materials about 3,000 tonnes dolomite refractory per 1 x 10^6 tonnes steel are being used and in the cement industry about 1,000 tonnes dolomite refractory/1 x 10^6 tonnes of cement.

Although detailed figures broken down into various categories of dolomite utilisation are available from only a few countries, Table III.I is a compilation of the most recent published data.

TABLE III.I - WORLD CONSUMPTION OF DOLOMITE

Country	Refractories	Sea Water Magnesia Process	Others Fertiliser Filler	Total Production	Crude	Calcined
Australia			30,000	400,000		
Belgium	320,000				2.6×10^6	330,000
Brazil	30,000			30,000		
Canada			100,000	2.6×10^6		
Eire		350,000		350,000		
Finland			80,000	80,000		
France	555,000			1.5×10^6		1.4×10^6
Greece		350,000		350,000		350,000
India	1.3×10^6			1.3×10^6		
Italy						1.2×10^6
Japan				3.0×10^6		
New Zealand			25,000	4.3×10^6		
Norway				600,000		600,000
Mexico				500,000		
Pakistan	40,000			40,000		
Portugal				55,000		
Spain				2.5×10^6		
Sweden	50,000		240,000	500,000	164,000	37,000
South Africa			225,000			
Turkey				450,000		
U.K.	250,000	500,000		8.3×10^6		
U.S.A.				700×10^6*		
West Germany	1.2×10^6			5.0×10^6	51.4×10^6*	616,000

* lime and dolomite

Figures collected from Board of Trade statistics and from Industrial Minerals 1976 and 1978.

Dolomite in Europe

Many European countries have exploitable deposits of dolomite but only a few possess the high qualities required for the sea water process or for refractories' production. Interest in the refractories side, particularly, has increased in recent years because only Austria and Greece have natural deposits of magnesite and only the U.K. and Italy produce refractory grade sea water magnesia (new plants are proposed for Eire, Greece and Netherlands). Dolomite is therefore an attractive alternative to magnesite many of the main European steel producers particularly if good, cheap, raw material is available near at hand.

Germany, Luxembourg, Belgium, France and the U.K. have all advanced technology on dolomite production and usage and permission to visit several of the major operations was kindly granted.

WEST GERMANY - The strata most extensively exploited for refractory grade dolomite in Western Europe are the Masselkalk levels in the Devonian sedimentary deposits. These form the southern flank of the Ardennes from Charleroi/Liege/Aachen and extend across the Rhine into Westfalen, north of Cologne (Koln) through Dortmund towards Hannover.

Dolomitwerke Wülfrath - is the largest producer of dolomite in West Germany and although the company has many interests in other areas, its main mining and producing complex is at Hagen-Halden near to Wuppertal and virtually within the Ruhr coal and steel-making districts. The company is a joint subsidiary of some of its major customers, August Thyssen-Hutte A.G. and Hoesch Werke A.G.

The company has a large quarry of consistent dolomite adjacent to the manufacturing complex which provides about 3×10^6 tonnes/year of rock, most of which is used as aggregate. A selected high quality material is produced for refractory manufacture at a rate of about 2400 tonnes/day. This is pre-crushed through a 25 mm screen and any size less than 6 mm, is removed. The graded rock is calcined in a rotary kiln, of which there are four - two with 350 t/day and two with 600 t/day output capacity - to a maximum temperature of 2000°C. The kiln construction permits a relatively slow burn to 1200°C to remove CO_2 followed by a fast rise to the maximum temperature. The total firing cycle is about 3-4 hours. The fuel used is pulverised coal, the ash of which contributes 0.5% Fe_2O_3 impurity to the product. This assists sintering.

Most of the dolomite which passes the 6 mm. screen is converted into sinter for iron ore treatment. A small proportion of -4 + 6 mm material is calcined at 1000°C and the product used for water treatment or for glass manufacture.

Large lumps of dolomite (50-110 mm) are mixed with coke and iron ore and sintered separately at about 1600°C in shaft kilns on another site.

The complete flow diagram is shown in Chapter V.

The main sintered product from the rotary kilns is crushed and carefully graded and used to produce bricks or blocks of dolomite refractory. Some of these are bonded with tar or pitch whilst others are direct ceramic-bonded by a refiring process.

Dr. W. Munchberg, Technical Director of Dolomitwerke Wulfrath kindly provided samples and gave much technical information concerning the raw material and its derived products. It was his opinion that the important characteristics of a dolomite for refractory manufacture should be as follows:-

1. Impurity level (SiO_2 + Al_2O_3 + Fe_2O_3) in the range 1 - 3% with a good balance between the three.

2. The impurities should be well distributed and no impurity mineral, particularly quartz, should exceed 20μ in size.
3. The diameter of the dolomite crystallites should be small and preferably should not exceed 100μ.
4. The porosity of the raw dolomite should be low and the pore size small in order to ensure adequate sintering.

Our test results on Hagen material are included in Table III.II These agree with the specifications provided by Dr. Munchberg.

Table III.II : Properties of Wulfrath (Hagen) Dolomite.

Chemical Analyses (Raw Dolomite)	SiO_2 0.5%		MgO	18-20%
	Al_2O_3 0.1		CaO	30-32
	Fe_2O_3 0.5		LOI	46-48
Crystallite Size	200 - 500μ			
Firing Changes	Raw Dolomite		Calcined	Full Sintered
Crystallite Size μ	200-500		<1	8-12
Porosity %	1-3		50	10-15
Pore Size μ	3		1	5

The principal uses of dolomite refractories manufactured by Wulfrath were:-

1.	Torpedo ladles - direct bonded		80%
2.	L.D. Converters		
	O.B.M. "	tar or pitch bonded	
	LDAC "		
3.	AOD Converters	direct bonded	
	VOD "		
4.	Ladles		
5.	Cement kiln		20%
	Dolomite kilns	direct bonded	
	Lime burning kilns.		

Trier Kalk at Wellen, mine by underground methods a Triassic dolomite which is part of the Paris basin deposition cycle. An almost identical deposit was also being produced across the River Mosel in Luxembourg by Refralux SARL. Both works were similar in size and in their calcined products.

The deposits were more or less horizontally bedded in strata which was rising steeply along the sides of the valley. The total thickness of dolomite was about 20 mts. but only the lower 10 mt. was good refractory quality although the upper level was extracted for aggregate or for fluxing purposes. To remove overburden would not be practical so the deposit was worked by room and pillar methods with roadways about 5 mts. wide.

The extracted dolomite was crushed into the size ranges:

0 - 6 mm for road stone, concrete.

6 - 40 mm. for a flux in steel manufacture

60 -120 mm for burnt dolomite.

The dolomite was burnt in shaft kilns at 1600^{o}C to make sintered dolomite for ramming mixes; at 1200^{o}C for fluxing applications.

The total plant capacity at both works was about 2500 t/day in four shaft kilns.

The analyses of the materials which we collected were:-

	CaO %	MgO %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	LOI %
Trier Kalk	29.1	21.4	1.5	0.9	0.4	46.7
Refralux	30.2	20.6	2.0	1.1	0.3	45.8

BELGIUM - Rocks of similar age (Devonian) to those at Hagen, West Germany and mined by Dolomitwerke Wulfrath,outcrop also in the Southern area of Belgium near to Philippeville. Because they are nearer the edge of the Ardennes uplift,the Belgian formations are more heavily contorted but they are lower in impurities than other occurrences and hence they are actively produced mostly for export to other European countries.

ProduitsDolomitiques de Merlemont - produces only crushed and graded raw dolomite at a rate of 1500 tonnes/day. Qualities with size ranges - 40 + 8 mm. and -8 mm. are generally marketed and about equal quantities of the two grades are produced.

The coarser grade is sold either to Valenciennes, France or to Wulfrath, West Germany for calcining. The finer grades are used in iron ore agglomeration, in fertilisers for glass manufacture and in soil beneficiation.

The samples collected have given the following analyses:-

SiO_2	0.08 - 0.21 %	CaO	30.2 - 30.8 %
Al_2O_3	0.19 - 0.28 %	MgO	22.4 - 22.9 %
Fe_2O_3	0.04 - 0.25 %	LOI	46.3 %

Other measured properties are included in a later chapter.

There are other producers of similar qualities in Belgium and 1978 figures show exports of over 1.75 x ^{6} tonnes.

FRANCE - Refractory grade dolomite is principally mined at Neau (Mayenne), about 100 Km. west of Paris. The formation is Devonian; it is quarried by the company Dolomie Francaise and the calcination capacity is about 200,000 tonnes/year. (950 t/day).

The chemical analyses of a typical sample collected from the Neau deposit was:-

CaO 31.2%; MgO 19.3%; SiO_2 0.83%; Al_2O_3 0.72%; Fe_2O_3 0.69%; LOI 47.2%.

At Neau, there are crushing and screening facilities to produce a -30 + 8 mm. quality for calcining and - 8 mm. for agriculture, glass-making, iron ore agglomeration etc. There are two rotary kilns, one 110 mt. long and 3.20 mt. diameter, the other 68 mt. long and 2.50 mt. diameter, together capable of producing about 600 tonnes/day of sintered product. There are also four shaft kilns which produce about 350 t/day of sinter calcined at about 1600°C or less.

About 50,000 tonnes/year of high quality calcined dolomite from Neau is transported to Flaumont (Nord) where an associated company, La Compagnie des Refractaires Basiques produces high quality bricks and blocks both pitch and ceramic-bonded in a fully automated plant which was completed in 1977.

Dolomie Francaise produces over 500,000 tonnes of dolomite per year for various applications. (See Table III.1).

EIRE - There is no production of dolomite refractories in Eire and although there are occurrences of dolomite, none that we have examined are sufficiently pure to be satisfactory for this purpose.

A deposit of Carboniferous dolomite is being mined by the Quigley Magnesite Division of Pfizer Chemical Corporation near Bennetsbridge, in Co. Kilkenny, calcined to comparatively low temperature, slaked and then used as a precipitant of magnesia from sea water. Because the magnesia so produced is used entirely for fertiliser and related products, high-grade material in terms of chemical purity is not essential.

An analysis of the dolomite being extracted at Bennetsbridge at the rate of 320,000 tonnes/year in September 1977 was:-

CaO 35.8%; MgO 14.8 %; SiO_2 0.8%; Al_2O_3 1.3%; Fe_2O_3 2.8%.

Another processing plant to recover refractory quality magnesia from sea water has recently been completed near Drogheda, Co. Dublin for Hepworth Ceramic Co. Ltd., but in the operation a high purity limestone will be used as a precipitant.

UNITED KINGDOM - There are many outcrops of dolomite material in the United Kingdom particularly in Carboniferous/Devonian strata levels but few of these are exploited as a source of refractory or high grade material although many are used as aggregates.

The important dolomites in England are confined to the Permian rocks which outcrop in the north on the coastline of County Durham and are exposed in a narrow band of surface rock formations in approximately a north-south direction. Valuable material is extracted in Durham, Yorkshire, Derbyshire, Nottinghamshire, with smaller amounts in Shropshire and Glamorgan.

Over 8.5 x 10^6 tonnes of dolomite is extracted per annum in England but most of this is aggregate quality.

The largest company to extract and process dolomite in the U.K. is the Steetley Co. Ltd. and the various divisions* of this company are involved in all aspects of dolomite technology. The Denniff group is concerned with the quarrying, preparation and marketing of aggregares; the chemical division controls the sea water magnesia process at Hartlepool which uses dolomite as a precipitant; minerals division in liaison with the refractories division produces and utilises the high quality material for use in brick and monolithic compositions.

The two main quarries for refractory or chemical grade dolomites are at Thrislington in Co. Durham and Whitwell, near Worksop in Nottinghamshire.

Typical analyses of these two main materials, the first of which is used as a precipitant for magnesia, the second for the production of refractories was as follows:-

Table III.III : Analyses of Steetley Dolomites.

	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	LOI
Thrislington	35.0	17.1	0.3	0.2	0.6	46.5
Whitwell	29.5	21.6	0.6	0.2	1.0	47.1

At Thrislington, the dolomite to be used in the precipitation of magnesia from sea water is firstly crushed and then calcined in a two stage rotary kiln to about 1200°C. The calcine is then hydrated but if the heating has been correctly carried out the resultant product is a mixture of MgO + $Ca(OH)_2$.

The quarry produces over 1 x 10^6 tonnes of material/year; the strata is about 10m thick and is near-horizontally bedded. Long-hole blasting loosens the rock which is then loaded into lorries by face shovels.

*Recently there have been changes in the structure of the Company so the divisions listed are no longer strictly correct.

The crushing and grinding plant is one of the most modern in the world. The main size reduction units are cone crushers which reduce run-of-mine material.

The coarser -5 + 1 cm material is screened and calcined whereas the finer dolomite is used for a variety of other purposes principally as a slagging or agglomeration material for iron-ore or in agriculture.

The calcined, partially slaked material is sent by rail to Hartlepool where the sea water magnesia plant is sited. This operation is described in a later chapter.

The Whitwell plant calcines dolomite in rotary kilns to 1800°C or above so that a good sinter is obtained suitable for manufacturing into refractories. High temperature calcination capacity is about 400,000 tonnes/year. The quarry operation is similar to that of Thrislington and so also is the comminution plant.

The calcined material is transported about two miles to the Worksop factory which manufactures over 130,000 tonnes/year of various basic refractories of which 40,000 tonnes are pitch and direct ceramic-bonded dolomites or saleable sintered grades.

Careful size selection and grading is absolutely essential to produce high quality shapes, achieved only by efficient screening and re-blending followed by pressing weighed batches of material to 10 tonnes/sq.in. or above.

Tar or pitch bonded products are prepared by mixing the hot graded dolomite with heated tar and then pressing into shape. Direct bonded dolomites are, firstly, pressed into shape with additives and then refired to 1600°C or above in tunnel kilns. These may then be dipped to impregnate them with tar. Further details are given in Chapter V.

Much of the technology is a closely guarded secret but sufficient test information has been forthcoming to predict whether or not Thailand materials would be suitable for dolomite refractory brick production.

Various monolithic formulations and ramming mixes are also manufactured by Steetley who also produce dolomite at Tafts Well Quarry in South Wales for use as fluxes etc., in the British Steel complexes at Port Talbot and Llanwen.

Italy, Norway, Sweden, Spain and Greece also produce dolomite (Table III.1) in considerable quantities but these countries have not been visited. Italy, Spain and Greece have a small production of refractory quality and the Grecian dolomite is sufficiently pure (less than 0.5% $SiO_2 + Al_2O_3 + Fe_2O_3$) to be used in the production of sea water magnesia. The Norwegian and Swedish dolomites, which are produced, are low in iron and are therefore much valued either for glass-making or as a filler/extender. Dolomite is used in Norway for the manufacture of magnesium metal. Both Scandinavian countries export a considerable proportion of their high-grade dolomites, crushed and sized into a large variety of grades.

Users of Refractory Dolomite

Dolomite belongs to the very limited class of materials which are capable of withstanding very high temperatures and at the same time resisting alkali conditions which are features of modern steel plant practices and of cement kilns. Its advantage is that it is considerably more common and cheaper than magnesia, but the lime which it contains cannot be stabilised by heat alone so that there is the constant problem of rehydration.

In recent years, improvements in technology have reduced but not eliminated the rehydration tendency and the modern high quality dolomite refractory has properties which make it superior to magnesia and other basic refractory compositions in some applications.

It is in Europe that dolomite technology and its consequent application is better developed than in most other areas and most steel plants in the major countries use dolomite refractories on a comparatively large scale. However, the amount of dolomite used relative to other alternative refractories varies widely in countries within the European Community. There are two main reasons a) the availability of indigenous dolomite of suitable quality and b) the relative price differential between dolomite refractories and those produced from magnesia and high alumina which may be regarded as technical alternatives.

In West Germany, for example, dolomite refractories of excellent quality are produced; there is no sea water magnesia production and high alumina materials have to be imported at considerable cost. Dolomite refractories have commercial advantages in many steel plant applications and about 150,000 tonnes/year of pitch and direct bonded bricks and shapes and monolithic compositions are used in a steel industry of 45.6 x 10^6 tonnes/year (i.e. 3.3 Kg/tonne).

The United Kingdom is fortunate in having indigenous sea water magnesia, access to relatively low-priced high alumina material and a supply of dolomite. About 40,000 tonnes of dolomite refractories are supplied to a steel industry of 23.0 x 10^6 tonnes (i.e. 1.7 Kg/tonne).

The situation is "fluid" and with the ever-increasing costs of imported raw materials and of energy, the future for dolomite refractories in those countries which have suitable resources looks very encouraging.

The above figures do not take into account fettling and patching grades, sintered dolomite used in slag modification or in iron-ore pelletisation.

The cement industry uses much less refractory than the steel industry but the situation is much the same. Dolomite, high alumina, magnesia-based compositions are all adequate and it is a commercial exercise to decide the preferred selection.

Dolomite refractories have been used in steel-melting furnaces since the early days of the basic open hearth furnace. Bricks, blocks and ramming mixes were used and because shut-downs were infrequent there were few problems with rehydration once the refractory was installed.

The new oxygen converters are more demanding in temperature and slag resistance but the selection of superior grades of raw material coupled with advances in the technology of manufacture have kept dolomite in the forefront as a basic refractory.

In some countries, e.g. the U.K., there has been a trend over the past five years to replace the all-dolomite linings of basic oxygen furnaces with either magnesia-enriched dolomite or magnesia itself. This trend has not been as rapid as predicted and in 1977 Leonard reported about 50% of LD-vessels were still lined with dolomite refractories and were presumably more economical to operate, even though there was a higher wear-rate than with magnesite.

In Belgium and West Germany, magnesite refractories have made even less inroads in their replacement of dolomite in LD vessels, but in Japan and the U.S.A., linings of such vessels are mainly magnesite.

Magnesite linings because of their great resistance to wear, allow greater furnace availability and less "down-time", but dolomite refractories may be only 25% of the cost of magnesia in some countries. Periods of recession in steel-making favour dolomite.

LD converters are likely to become the main steel producing unit in Thailand and other parts of S.E. Asia over the next few years and if suitable tar-bonded dolomite refractories or doloma enriched with magnesite are available they would satisfy the lining requirement to the exclusion of imported magnesites.

Electric Arc Furnaces are also important steel production units. In West Germany and Belgium, direct-bonded dolomite blocks are the principal hearth materials and comprise a large percentage of the total tonnage of refractories. At the slag line, magnesite or chrome-magnesite are preferred. In recent years roofs in rammed dolomitic materials have been successfully installed. In the U.K. and elsewhere in the world, magnesite-based refractories are preferred throughout the E.A.F. because the cost differential of dolomite is not so great.

Electric Arc furnaces are the main steel-making furnaces employed in Thailand at the present time. They use imported magnesia-based refractories most of which could be replaced by indigenous dolomite qualities.

Argon-Oxygen Decarbonisation (AOD) process is the main method of producing stainless steels.

The newer units of the steel industry involving gaseous injection or vacuum degassing require a basic lining to withstand the prolonged and sometimes violent contact with metal and slag. Direct-bonded dolomite bricks have proved superior in economic importance to all others in these applications particularly in European countries.

Steel Ladle practice is changing and more "work" on steel quality control is being carried out in these vessels than was the practice when simple filling of ingot moulds via a stopper assembly was their only function. Holding times of steel in ladles may be more than double particularly when continuous casting is employed. Doloma-based direct-bonded refractories are proving to be exceptionally good as lining materials in modern ladle practice. They are commonly employed in West Germany and their use is increasing in the U.K. Peatfield and Spencer claim that doloma cuts refractory costs, reduces erosion rates, is resistant to spalling and to basic slag attack and furthermore any losses from the refractory will not adversely affect slag composition. Either fired, ceramic-bonded bricks or tempered pitch-bonded bricks are preferred but experiments are proceeding on rammed doloma linings.

Slag additions of dolomite have brought about some of the most remarkable improvements in steel practice in recent years.

It was predicted from equilibrium diagram studies that lime slags would dissolve magnesia from vessel linings until saturation occurred, but above this point there would be little or no chemical reaction.

Additions of relatively soft-fired dolomite (which is thus chemically reactive) to the lime normally added to produce slag has improved vessel lives dramatically and this has become standard practice in most BOS operations. The amount of dolomite which is added to the slag is critical and ideally should be in the range 25-30 Kg/tonne of steel which corresponds to about 6% MgO in the slag. Under these conditions chemical attack on the lining refractory (which contains MgO) is virtually eliminated and the more viscous slag confers other advantages. The result of these additions has been fully documented in the U.S.A. and Japan and has shown that BOS lining lives have been increased from about 400 to over 5000 with a reduction in refractory consumption from around 6 Kg/tonne steel to about 1.5 Kg/tonne steel.

The addition of such large amounts of dolomite to the slag does not meet with universal approval. Only material with a very low impurity content - particularly silica - is acceptable and the cost of this in many countries is prohibitive.

In Thailand, high quality dolomite is plentiful and it would be a safe prediction that the primary steel furnaces planned for the early 1980's would use the optimum dolomite slag addition (20-25 Kg/tonne of steel) and line the vessels with tar-bonded doloma bricks which would be required at about 2.5 Kg/tonne of steel.

If a sea water magnesia plant is constructed and the steel industry follows European trends, enriched doloma with magnesia is likely to be the preferred refractory which would reduce slightly the total quantity required but the opportunities for substantial exports would increase as a consequence.

Price Structure

Our researches into production and usage of dolomite refractories in Europe and elsewhere revealed that the economic aspects varied within each country and governed the extent of their application in some cases to a greater degree than technical merit.

Dolomite must compete with magnesia and frequently with high alumina qualities and much depends on the relative price of each. At the present time there is so much variation month-by-month in some imported costs that a true picture is difficult to derive.

In general terms, good dolomite from indigenous sources is available in most of the countries in W. Europe at a relatively low cost. The material is less available near to steel-making areas in U.S.A. and Japan. Magnesia is produced in the U.K. but only in Italy of other European countries. Greece and Austria have deposits of magnesite but France and West Germany rely on imported materials. U.S.A. and Japan produce high quality sea water magnesia and the former has high alumina raw material. High alumina material from calcined bauxites has to be imported into Europe from Guyana, Surinam or China and prices for good calcined quality are escalating.

In the European zone, dolomite costs (Jan. 1st 1980) were approximately as follows:-

	£/tonne (ex works price)
Quarried and rough graded	1.70
Pulverised and size controlled	4.50 - 10
Soft-fired	30 - 40
Dead-burned (doloma)	35 - 45

Best quality raw dolomite pulverised and graded for the glass and filler industries is quoted in the range £20-100/tonne.

Dead-burned magnesia is £120-150/tonne (ex works price) and calcined alumina £118/tonne C.I.F. European Port. Transport, duty etc. have all to be considered in the delivered price. From private figures which have been given the relative prices of each competitive refractory grade is as follows:-

	Dolomite	Magnesite	High Alumina
U.S.A.	1	1.5	1.6
Japan	1	1.4	1.8
U.K.	1	2.1	2.4
West Germany	1	3.2	3.6

This is not the whole story, because the "life" of the refractory and the "down-time" for repairs and replacements need to be fitted into the equation but it can be concluded that where dolomite has a large price advantage - as it would in Thailand and S.E. Asia - many uses will be found for it in refractory applications.

CHAPTER IV

PROPERTIES OF THAILAND AND OTHER DOLOMITES

Dolomite is a mineral which is relatively abundant throughout Thailand, (Chapter II) but the deposits suitable as a raw material for refractories must not only be large and close to a consumer but must also possess a consistent chemical and mineralogical analysis, low in impurity and have physical properties which enable it to be sintered to a high density.

The following properties of dolomite were therefore measured and investigated:-

1. Appearance and general properties.
2. Chemical Analysis.
3. Microstructure analysis.
4. Differential Thermal Analysis (DTA).
5. X-Ray Diffraction Analysis (XRD).
6. Bulk Density, True Density and Porosity.
7. Changes in these properties on heating to various temperatures.

Chemical Analysis. Standard methods were used for the chemical analyses of dolomites but mostly they involved the new atomic absorption unit (A.775 Tectron) which was purchased for the research and has proved invaluable.

The analyses have been reported in Chapters II and III but reference must be made to a staining method which was used to identify quickly dolomite samples in the field.

It was difficult to differentiate between limestone and dolomite in many of the Thailand exposures so a field kit was devised based on a staining technique attributed to Warne.

The preliminary test on a broken rock fragment involved adding it to dilute hydrochloric acid in a suitable bottle. Effervescence indicated a carbonate rock, otherwise the rock was discarded.

The sample was withdrawn and washed with fresh water and then immersed in a solution of Alizatin Red S. If the material were calcite a deep red stain developed on the surface quite quickly; dolomite did not take the stain and with a little practice positive identification was easy.

This method proved most useful and saved considerable time. The small field kit which was devised could be carried to the outcrop areas. It has been extended to differentiate between and identify all the major carbonate rocks.

<u>Microscopic Analysis</u>

Both conventional and electron microscopes have been used to measure several important characteristics of Thailand dolomites in comparison with European materials which are in industrial use.

<u>Transmitted Light</u> analyses showed clearly the nature of impurities which were present. Not only were the main types identifiable but also their size and distribution which are so important in fi. ng reactions.

In every case examined the main impurities could be identified as quartz occurring as small pegmatite veinlets or stringers between the dolomite crystallites (Fig. IV.I). The impurity particles ranged from 1-2 microns in Kanchanaburi material to + 20μ in Satun material. Iron-staining was also

Fig. IV.1. - PHOTOGRAPH SHOWING QUARTZ PEGMATITE VEINLET IN DOLOMITE

(Magnification x 340)

observed in some specimens associated with the veinlets of quartz. In one sample, namely KPL from the Kanchanaburi area a white fine-grained powdery impurity was noted which proved to be talc.

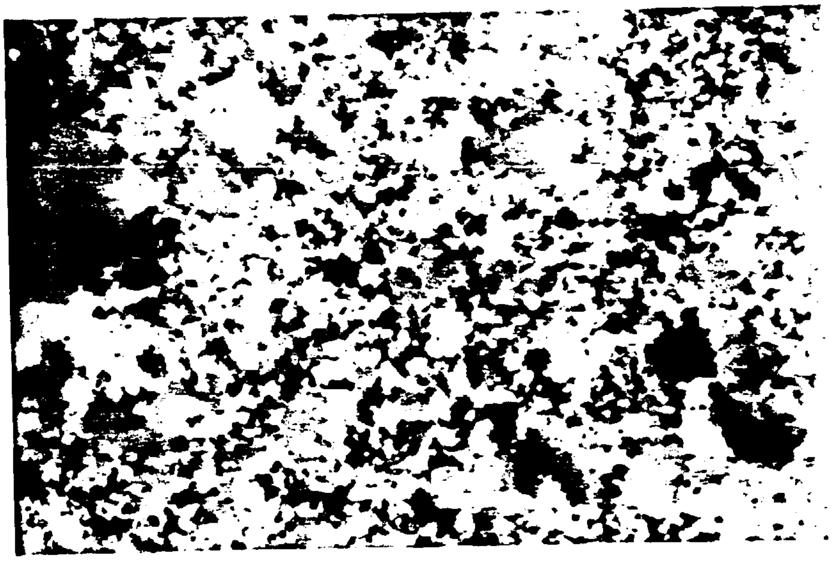
In all Thailand dolomites, including those from the Songkhla/Satun area where the impurity level was high, the pegmatite veinlets were composed of small crystallites which should react quickly and completely with the dolomite at high temperatures. This would result in efficient sintering.

Reflected Light analysis was used to identify the actual crystallites of dolomite under polarised light. Careful polishing was vital to secure clarity of grain but, once the technique had been mastered, the crystallite size could be established with accuracy using a calibrated scale in the eyepiece of the microscope which was a Vickers M.55. The other important feature shown under reflected light was the size and distribution of pores.

Photomicrographs of dolomite specimens in reflected light showing the features of crystallite size and pore size are in Fig. IV.2, a b c d e f g h and the relevant parameters in Table IV.1.

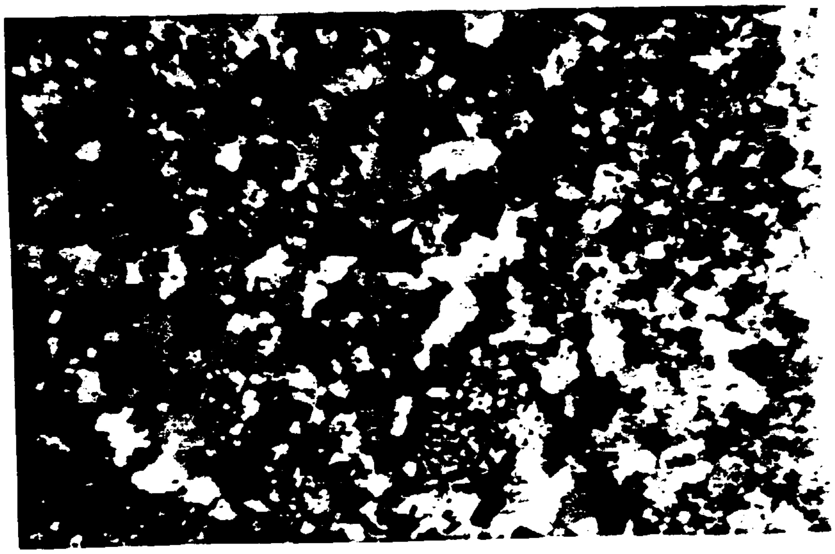
One interesting point has emerged from microscopic examination which has so far not been fully explained. Dolomite from Ko Si Chang is composed of twinned crystals (Fig. IV.2d) whereas all other samples showed no twinning whatsoever.

The crystallite sizes of the dolomites showed substantial differences. Merlemont, Belgium material was the largest with 200 microns but most of the Thailand dolomites were composed of small crystallites about 75-100 microns. Thailand material was similar to Wulfrath dolomite and was obviously heavily metamorphosed. Whilst



a. Kanchanaburi KS

X 74



b. Kanchanaburi KMN

X 74

c. Ratburi RKW

X 42

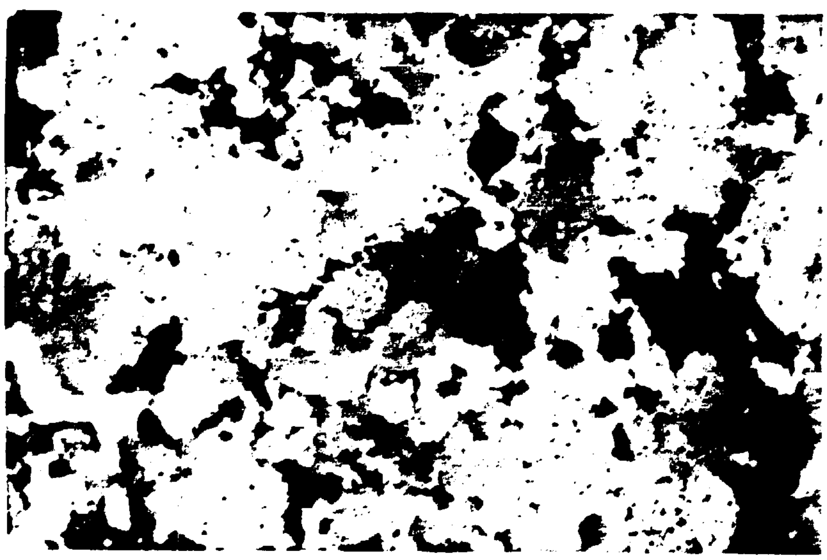
Fig. IV.2. a, b, c. - POLISHED SECTION OF RAW DOLOMITES

d. Ko Si Chang KSC

× 74

e. Songkhla SKL

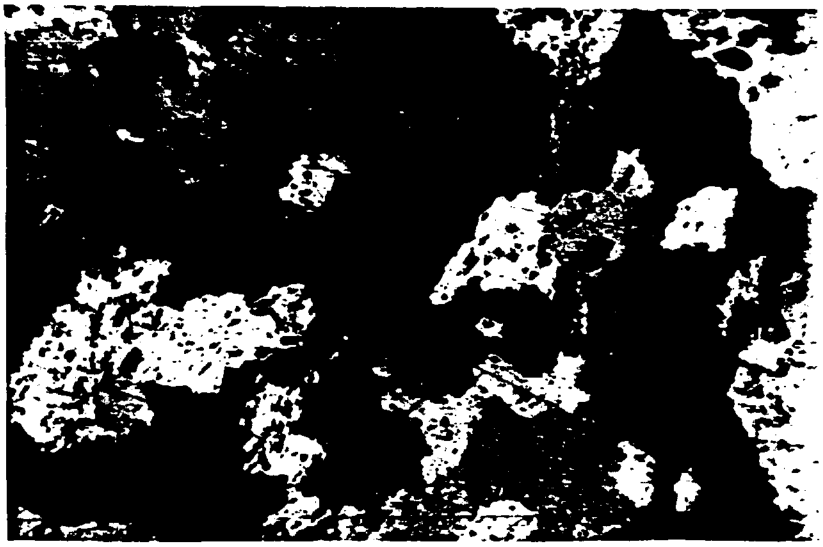
× 74



f. Whitwell WW

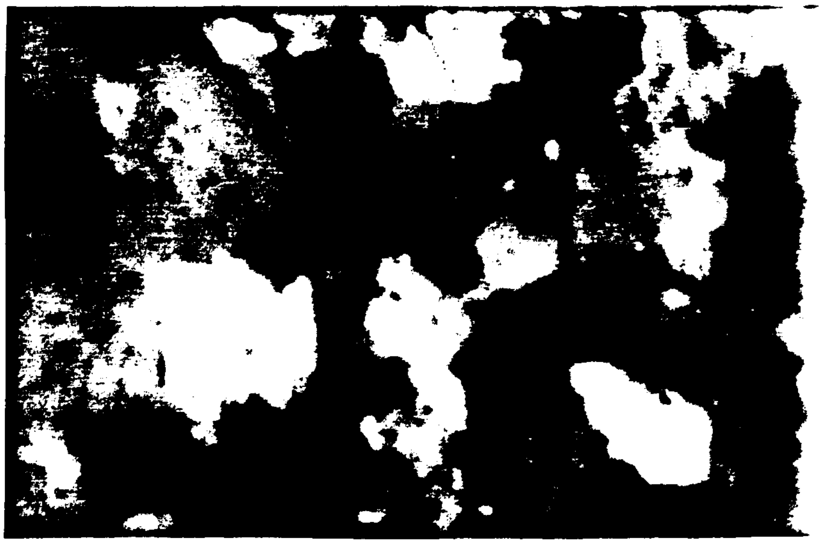
× 74

Fig. IV.2. d, e, f. - POLISHED SECTION OF RAW DOLOMITES



g. Wulfrath WF

X 42



h. Merlemont MM

X 42

Fig. IV.2. g, h. - POLISHED SECTION OF RAW DOLOMITES

TABLE IV.1. - PROPERTIES OF SELECTED DOLOMITES

Properties	KS	KMN
Colour	White to very light grey	White to Yellow-ish
Texture	Fine	Fine to Medium
Hardness		
Moh's Scale	3-4	3-4
Crystallinity by X-Ray and Microscope*	C	C
Crystallite Size and Shape		
Mean Micron	75	30
Shape	Rhombo-hedral(R)	R

* Well Crystalline

RKW	KSC	SKL	WW	WF	MM
dark grey	dark grey	dark grey	buff to light brown	dark grey	light grey
Fine	Granu-lar	Fine	Earthy	Fine to Medium	Medium to Granular
3-4	3-4	3-4	3-4	3-4	3-4
C	C	C	C	C	C
100	200	150	75	200	200
R	R	R	R	R	R

U.K. was much less consolidated with a more porous structure and a different grain configuration.

The Scanning Electron Microscope enabled the fractured surface of specimens to be examined at high magnifications (up to 10,000 times) but with considerable depth of focus. The characteristic rhombohedral shapes of dolomite and their plate-like nature were clearly revealed (see Fig. II.3).

Mineralogical Tests

Both Differential Thermal Analysis and X-Ray Analysis were used to compare the mineralogy of the selected Thailand and European samples.

D.T.A. confirmed the nature of dolomite (Fig. IV.3); although the results were similar there were interesting points of difference which have not yet been explained.

X.R.D. is the method most commonly used for mineral identification and analysis and also for studying changes that take place on firing.

Table IV.II is a compilation of the major dolomite spacings in all samples under investigation. The purity of the dolomite was established clearly.

In some samples other lines in the X.R.D. pattern were noted which corresponded with impurities such as calcite and quartz.

Physical Properties

The physical properties of dolomite, particularly the true and bulk densities, porosities and pore sizes and their changes on firing are at least as important as chemical and mineralogical characteristics in determining the suitability of the material for industrial use.

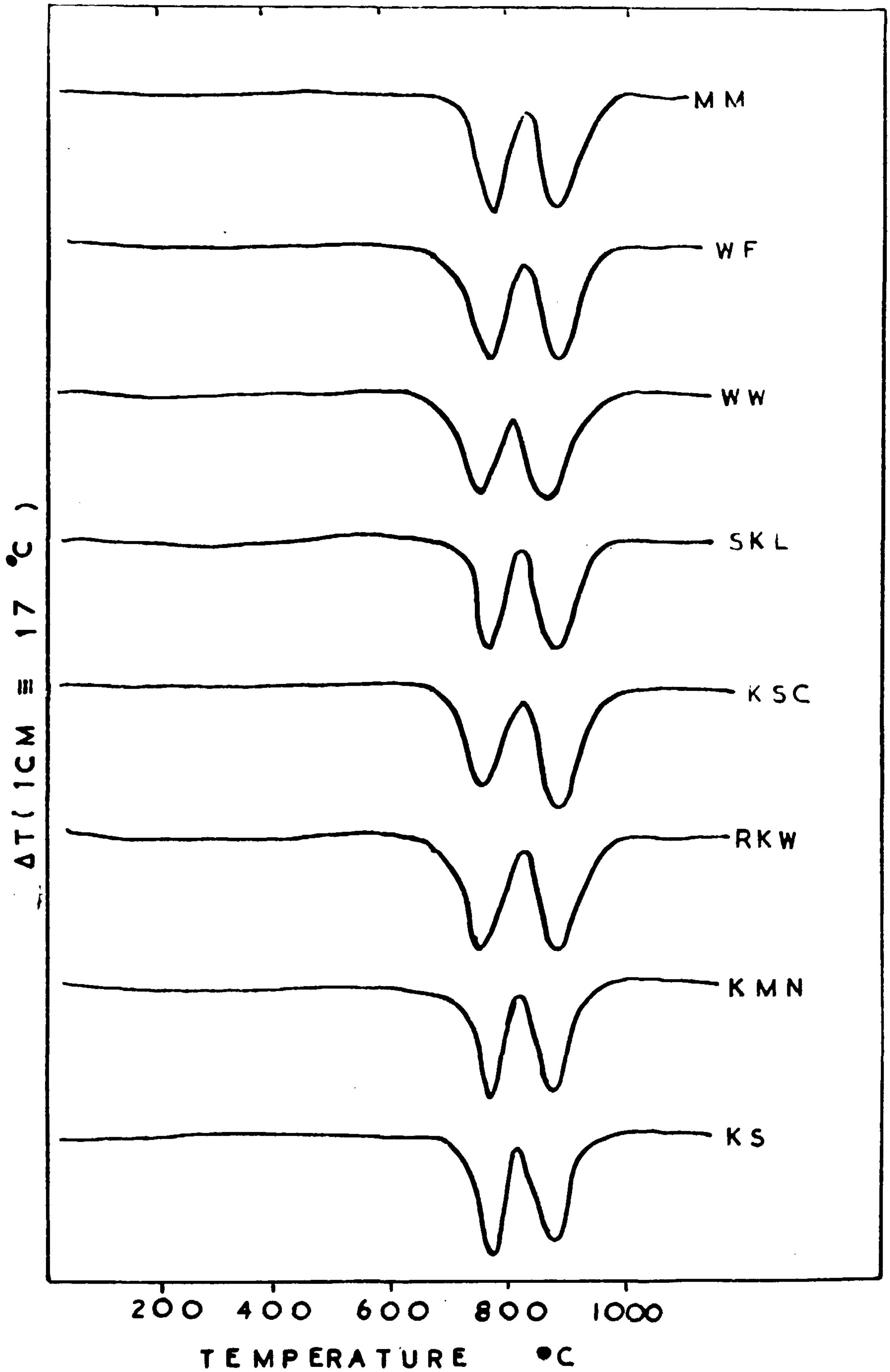


FIG IV. 3. THERMAL CURVES OF DOLOMITES

TABLE IV.II - X-RAY DIFFRACTION PATTERNS OF DOLOMITES.

d-spacing A°	ASTM st	BS st	KS	KMN	RKW	RKS	SKL	WW	WF	MM
4.03	3	3.8	3.8	3.8	2.8	2.2	3.8	3.6	2.9	3.5
3.69	5	7.1	6.0	6.3	6.5	5.7	6.7	5.5	6.3	6.0
2.89	100	100	100	100	100	100	100	100	100	100
2.67	10	9.6	12.6	13.0	12.3	10.6	9.7	9.8	14.2	12.4
2.54	8	8	8	8	8	8	8	8	8	8
2.41	10	12.1	9.2	9.9	8.9	9.2	9.7	11.9	7.3	7.7
2.19	30	26.8	28.6	30.00	28.3	20.3	+28.6	25.5	26.3	26.3
2.07	5	5.4	4.5	4.6	4.6	2.0	3.8	3.6	3.0	3.0
2.02	15	18.3	17.9	18.7	11.5	11.8	12.7	11.9	13.7	14.9
1.85	5	4.8	4.0	4.5	3.8	1.8	3.2	3.0	3.0	3.2
1.81	20	21.8	26.3	26.9	25.8	23.7	26.0	23.7	27.7	28.3
1.79	30	24.6	26.8	27.6	26.5	19.1	23.5	21.9	24.7	26.0
1.567	8	3.8	3.4	3.5	3.2	2.5	2.7	2.7	2.8	1.3
1.545	10	8.2	9.2	7.0	6.5	3.5	3.2	4.4	5.0	2.9
1.496	1	1.2	1.2	1.4	1.2	1.7	1.7	1.2	1.0	1.6
1.465	5	5.8	5.6	6.2	5.1	4.9	4.7	-	-	5.2
1.445	4	2.9	7.2	7.5	8.2	20.3	11.0	7.9	13.7	7.6
1.431	10	16.8	15.7	16.6	15.5	17.5	15.9	14.8	18.0	16.2
1.413	4	2.0	1.5	1.6	1.5	1.7	1.6	1.5	1.7	1.9
1.389	15	6.3	5.5	5.1	5.1	3.4	4.0	3.0	5.3	4.0
1.335	8	3.8	5.0	5.0	5.1	7.1	5.9	6.0	5.3	5.1
1.297	2	1.9	2.2	2.6	2.2	1.8	1.6	1.5	2.2	1.9
1.269	2	2.5	2.3	2.6	2.2	2.6	2.4	2.2	2.3	2.2
1.238	5	2.8	3.1	3.5	3.0	2.3	2.4	2.2	2.4	2.0
1.202	3	1.2	1.1	1.1	0.9	0.8	1.0	0.9	1.0	0.9
1.168	4	2.2	3.2	3.2	3.1	2.8	3.3	2.5	2.8	2.7

Figures quoted are relative intensities of the line.

The results of the measurement of the physical properties of raw dolomite are in Table IV.III. The calcined chemical analyses are also included in this table for comparison purposes.

TABLE IV.III - PROPERTIES OF DOLOMITES

Sample	Chemical Analyses (calcined)						Physical Properties			Crystallite Size μ(mean)
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	LOI	True*	Bulk*	Porosity	
KS	59.7	39.8	0.42	0.04	0.15	47.0	2.84	2.84	0.0	75
KMN	59.1	39.2	0.67	0.04	0.08	47.0	2.86	2.86	0.0	80
RKW	59.4	39.9	0.25	0.04	0.55	47.0	2.83	2.79	1.4	75
KSC	59.8	34.8	2.38	1.95	1.09	43.9	2.78	2.76	0.8	200
SKL	56.4	32.2	8.57	1.18	1.48	45.1	2.76	2.66	3.6	150
Steetley UK	56.8	40.8	1.00	0.40	1.00	46.5	2.78	2.68	3.6	75
Wülfrath Ger.	59.5	39.0	0.98	0.32	1.00	46.5	2.82	2.80	0.7	220
Merlemont Bel.	57.0	42.1	0.20	0.45	0.34	45.8	2.81	2.78	1.1	200
Neau, France	58.2	38.0	1.60	1.40	1.30	47.2	2.81	2.74	2.6	170

KS Kanchanaburi (Khao Laem) KMN Kanchanaburi (Kamnam)

RKW Ratburi SKL Songkhla

KSC Ko Si Chang

It may be concluded that KS, KMN and RKW dolomites have excellent physical characteristics which compare favourably with German and Belgium materials. Both KSC and SKL dolomites have lower values of true densities - probably because of relatively high impurity values - and bulk densities - due to a higher porosity. However, these still compare favourably with Whitwell, U.K. material from which excellent refractories are manufactured.

FIRED PROPERTIES

To be of industrial value in the manufacture of refractory grades, dolomite must be fired to high temperatures to complete all chemical reactions and to produce a highly sintered product which is capable of withstanding intense heat and resisting corrosive slags and gases.

During the firing process, there are two critical temperature ranges. The first from about 800 - 1200°C is the region in which the mineral decomposes with the loss of carbon dioxide and harmful sulphur. Almost 50% of the total weight is lost in this region; the crystal lattice and rock texture are broken down and complete disruption may occur. If the rate of decomposition is too great and the stresses become excessive the rock fragments expand and shattering will occur. In extreme cases, the material is reduced to a powder and it would then be virtually useless for calcining further. In recent years, American practice has overcome this problem; the powdery low-temperature calcine, which is highly reactive, is pressure-briquetted and the agglomerates can then be sintered at very high temperatures to extremely dense fragments. However, the more usual practice is to calcine dolomite in one firing process either in a shaft or rotary kiln and, under these conditions, rock disintegration can be a serious problem.

The second critical temperature range is the final sintering stage which takes place between 1600 - 2000°C. Until these temperatures are attained calcined dolomite is prone to rapid hydration, it is highly porous and lacking in strength. The sintering conditions result in crystal growth of the periclase (MgO) phase and to chemical combination of the lime component with the impurity oxides. The greater the content of impurities, the easier it is to densify the calcined mass but the poorer will be the quality of the final sinter. In modern technology of dolomite, the trend is to use the purest grades of rock and accept that high temperatures and prolonged sintering will be essential; but for qualities required for less arduous duty, impurities, such as iron oxide, are frequently deliberately introduced to increase the ease of sintering.

The criteria of good sintering are high bulk density, low porosities and good inter-linking between the various crystal phases some of which crystallise from a liquid when the sinter is cooled.

Low temperature firing properties

The selected Thailand dolomites were tested under standard conditions with European qualities in the temperature range 1000°C - 1400°C and properties of importance measured. These results are included in Tables IV.IV and IV.V.

The abradability values of both Ko Si Chang (KSC) and Ratburi (RKW) dolomites were appreciably higher than other materials and both would probably be difficult to calcine in rotary kilns without large losses of fine material.

The Kanchanaburi materials (KS and KMN) were excellent and should present no problems in any calcining technique.

High temperature firing properties

When fired to sintering temperatures (1600-2000°C), dolomites are composed of MgO (periclase), lime (CaO) and various compounds of lime with alumina, silica and iron oxide. A liquid phase develops which increases in quantity with the maximum temperature of firing and from this phase, various compounds crystallise on cooling.

TABLE IV.IV. - CALCINING CHARACTERISTICS OF DOLOMITE AT LOW TEMPERATURES

TEMPERATURE °C

SAMPLE	1000°C			1200°C			1400°C		
	True Δ	Bulk Δ	% Porosity	True Δ	Bulk Δ	% Porosity	True Δ	Bulk Δ	% Porosity
KS	3.40	1.80	47.1	3.45	1.81	47.5	3.41	1.91	44.0
KMN	3.36	1.78	47.1	3.47	1.83	47.3	3.42	1.86	45.0
RKW	3.35	1.69	49.6	3.45	1.76	49.0	3.47	1.85	46.7
KSC		n.d.			n.d.		3.21	1.97	38.6
Whitwell UK	3.33	1.64	51.5	3.39	1.56	54.0	3.52	1.87	46.9
Wülfrath Ger	3.39	1.43	57.8	3.41	1.65	51.6	3.48	1.65	46.0
Mariemont Bel	3.43	1.68	51.0	3.42	1.72	49.7	3.51	2.01	42.7
Bernotsbridge Eire	3.44	1.59	53.8	3.47	1.63	53.[illegible]	3.48	1.70	51.9

KSC samples were too fragile to test below 1400°C.

TABLE IV.V. - CALCINING CHARACTERISTICS OF DOLOMITE AT LOW TEMPERATURES

TEMPERATURE OF FIRING °C

SAMPLE	1000°C			1200°C			1400°C		
	% Abr.	% CO_2	% S	% Abr.	% CO_2	% S	% Abr.	% CO_2	% S
KS	6.9	0.54	0.004	4.4	0.37	0.000	4.1	0.28	0.000
KMN	4.6	2.52	0.000	11.6	0.39	0.000	4.9	0.33	0.000
RKW	[illegible]	1.00	0.025	4.8	0.32	0.008	8.5	0.47	0.005
KSC	53.6	0.28	0.057	65.0	0.14	0.030	33.1	0.13	0.023
Whitwell UK	12.2	0.55	0.031	5.8	0.31	0.004	6.1	0.18	0.001
Wülfrath Ger	8.5	0.47	0.000	5.7	0.27	0.000	4.8	0.10	0.000
Merlemont Bel	33.8	0.36	0.011	14.4	0.15	0.007	15.1	0.07	0.000
Bennetsbridge Eire	7.9	0.69	0.015	4.6	0.41	0.005	3.6	0.21	0.002

Footnotes: There was insufficient sample of SKL (Songkhla/Satun) to complete these tests.

% Abr. = % abrasion under standard test.

These reactions cause sintering and densification in calcined dolomite and largely determine its potential industrial value.

These changes in Thailand dolomite were investigated fully. The composition of the materials after firing to various temperatures was studied by X-ray methods and under the microscope and the physical properties also measured.

X-Ray diffraction patterns have been produced from all samples at temperatures from 1600°C upwards. Time has not permitted a full analysis to be completed as yet but typical series (KMN and Wulfrath) are shown in Tables IV.VI. The characteristic lines of MgO and CaO are marked; the other lines correspond to interstitial minerals. It will be noted that after the higher temperatures of firing, the intensities of the lines corresponding to CaO become decreased and, to a lesser extent, so does the line pattern of MgO, but the ancillary mineral content increases.
Microscope tests particularly of reflected light sections and fracture surfaces in the scanning electron microscope have also proved most interesting in revealing the changes in structure which are produced on firing. An illustration of these results is in Fig. IV.5.
Physical Properties of dolomites fired up to 1800°C are shown in Table IV.VII .

In general the dolomites from the south of Thailand sintered and densified at low temperatures because of their high impurity level, whereas the purer varieties from the north densified less readily, and some would probably be unacceptable because they are too pure.

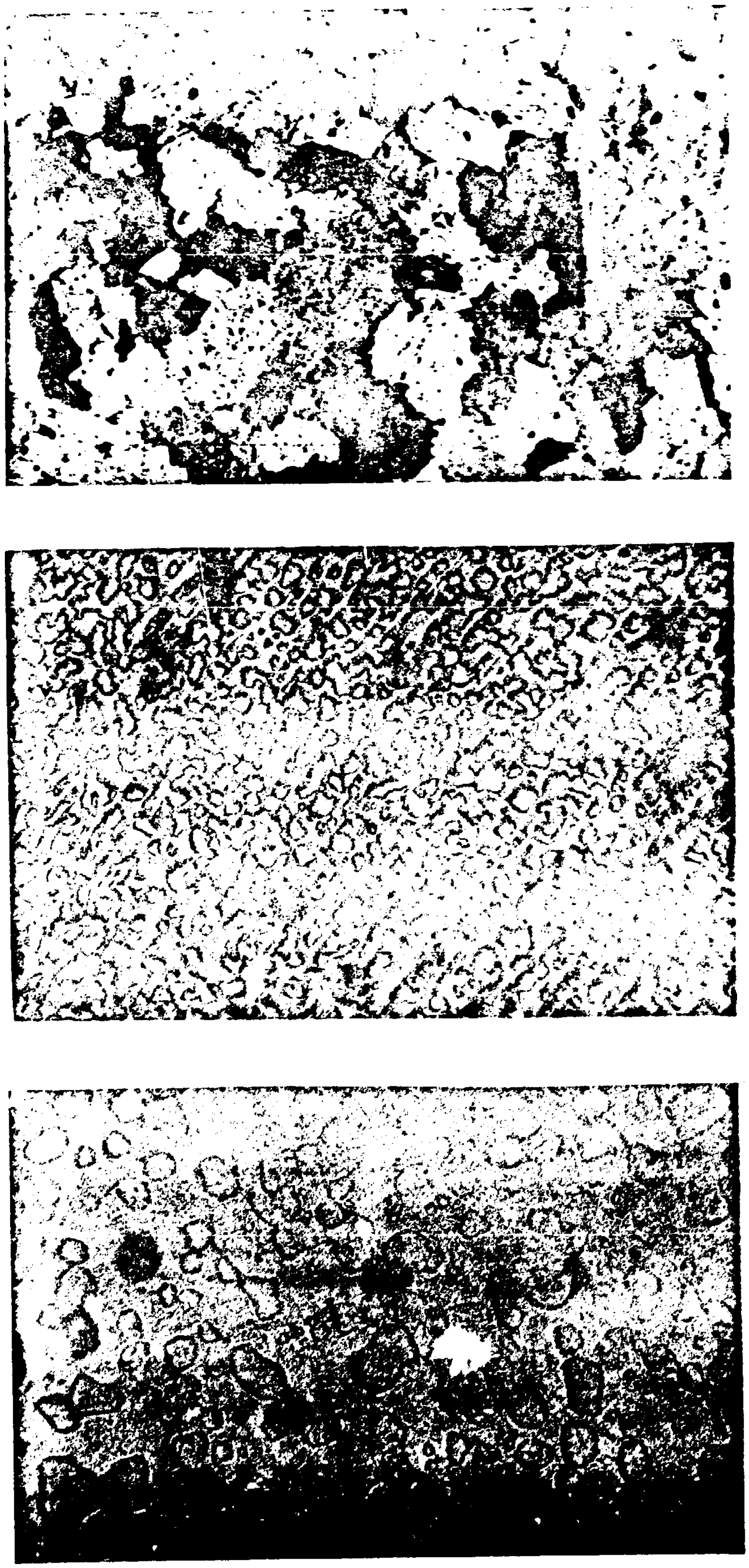
The materials from the Kamnan area and from Ko Si Chang have considerable potential. The former would need to be calcined at 1800°C but it would then densify adequately and it is exceptionally pure. The latter would be easier to treat and would be acceptable for medium duty use.

d-spacing A°	Relative Peak Height				Likely Phase
	KMN 1500°C	KMN 1600°C	KMN 1700°C	KMN 1800°C	
3.105				3.0	
3.043				2.5	
2.771-2.778	>93	> 93	> 93	88.0	CaO
2.684-2.686	2.5	-	-	3.0	
2.614	2.5	-	-	7.0	
2.429-2.433	13.5	15.0	16.5	15.0	MgO
2.401-2.398	> 94	> 94	> 94	> 93	CaO
2.338	12.5	14.5	24.0	20.0	
2.217	-	-	1.5	-	
2.181	-	-	2.0	-	
2.105	> 95	> 95	> 95	> 93	MgO
2.024-2.025	23.5	26.0	31.5	30.3	
1.933	-	-	-	2.5	
	-	-	-	-	
	-	-	-	-	
1.762	-	-	-	2.0	
1.699-1.700	>96	>96	>96	> 93	CaO
1.490	50.5	52.8	58.0	59.5	MgO
1.451	33.0	32.0	33.5	35.5	CaO
1.433	42.0	45.5	50.0	53.5	
1.388	33.5	29.5	32.5	27.8	CaO
1.271	7.2	6.5	7.0	7.0	MgO
1.221-1.222	41.5	42.6	50.0	50.5	MgO
1.201-1.203	12.8	12.0	12.0	11.0	CaO
1.103	11.2	10.3	11.3	9.0	CaO
1.072	31.0	28.5	32.0	25.0	CaO
1.055	5.0	6.0	6.0	6.5	MgO
1.01	-	2.5	-	2.0	
0.981	23.0	20.7	22.5	18.0	CaO
0.965	2.5	2.3	3.2	2.5	MgO
0.941	14.5	14.0	16.8	19.0	MgO

TABLE IV.VIa- RELATIVE INTENSITIES OF X-RAY DIFFRACTION LINES OF FIRED SAMPLES OF KMN DOLOMITE

d-spacing A°	Relative Peak Height				Likely Phase
	WF 1500°C	WF 1600°C	WF 1700°C	WF 1800°C	
3.121	-	-	3.5	-	
3.038	-	-	4.2		
2.889	-	-	17.5	-	
2.776-2.789	> 92	> 93	69.5	66.5	CaO
2.694-2.698	-	-	6.0	7.0	
2.610-2.614	-	-	3.5	5.0	
2.429	16.0	16.0	16.0	13.0	MgO
2.398-2.402	> 92	> 93	> 95	> 97	CaO
2.338	16.5	13.5	20.0	20.0	
2.186-2.191	-	-	8.0	2.5	
2.105-2.106	> 94	>.94	> 93	92	MgO
2.025-2.029	25.5	25.3	27.0	36.5	
1.981	-	-	-	1.6	
1.907-1.915	-	-	3.5	2.2	
1.829	-	-	-	2.0	
1.766	-	-	-	2.0	
1.699-1.701	> 95	>.95	> 93	88	Ca
1.630-1.634	-	-	3.5	2.0	
1.489-1.490	57.0	64.0	60.0	47.5	MgO
1.450-1.451	37.0	37.5	30.0	22.5	CaO
1.434	43.0	48.0	46.5	62.5	
1.388-1.390	37.0	34.0	27.0	22.3	CaO
1.270-1.271	9.0	9.0	6.2	6.5	MgO
1.221-1.223	41.0	44.5	43.4	57.5	MgO
1.202-1.203	15.5	14.5	10.5	[illegible]	CaO
1.103-1.104	13.0	13.5	10.0	7.5	CaO
1.075-1.076	37.8	36.0	26.5	19.2	CaO
1.053-1.054	7.0	8.0	7.0	6.0	MgO
1.010	-	-	-	2.0	
0.981	20.0	25.0	19.0	14.0	CaO
0.966	4.5	3.0	3.0	3.0	MgO
0.941	20.0	21.0	16.0	14.0	MgO

TABLE IV.VI 5 - RELATIVE INTENSITIES OF X-RAY DIFFRACTION LINES FOR FIRED SAMPLES OF WULFRATH DOLOMITE



RAW

X 74

FIRED, $1700^{0}C$

X 600

FIRED, $1800^{0}C$

X 600

Fig. IV.5. - CHANGES IN MICROSTRUCTURE OF DOLOMITES ON FIRING.

TABLE IV.VII - PHYSICAL PROPERTIES OF FIRED DOLOMITES

Sample	Raw			1500°C			1600°C			1700°C			1800°C		
	True Δ	Bulk Δ	% Por	True Δ	Bulk Δ	% Por	True Δ	Bulk Δ	% Por	True Δ	Bulk Δ	% Por	True Δ	Bulk Δ	% Por
KS	2.84	2.84	0.0	3.37	2.00	40.7	3.35	2.09	37.6	3.48	2.65	23.9	3.48	3.03	12.9
KMN	2.86	2.86	0.0	3.35	1.89	43.6	3.35	2.09	37.6	3.38	2.60	23.1	3.48	3.12	10.3
RKW	2.83	2.79	1.4	3.20	1.71	46.6	3.28	2.25	31.6	3.35	2.57	23.3	3.38	2.72	19.5
KSC	2.78	2.76	0.8	3.23	2.23	31.0	3.19	2.46	22.9	3.41	2.94	16.7	3.47	3.06	11.8
SKL	2.76	2.66	3.6	3.36	2.17	35.4	3.40	2.61	23.2	3.33	3.05	8.4	3.33	3.00	9.9
WW	2.78	2.68	3.6	3.40	2.04	40.0	3.38	2.31	31.7	3.40	2.85	9.1	3.49	3.08	11.8
WF	2.82	2.00	0.7	3.38	1.96	42.0	3.37	2.44	27.6	3.41	2.93	14.1	3.40	3.21	5.6
MM	2.81	2.78	1.1	3.42	2.61	23.7	3.45	2.64	23.5	3.46	3.09	10.7	3.46	3.13	9.5

The low iron oxide content of many Thailand dolomites is of interest because as a consequence their refractory qualities could be exceptionally good if they can be calcined at a sufficiently high temperature to obtain a good sinter. Undoubtedly, if dolomites of this quality were to be available in Europe they would be highly prized and a new technology might develop around them.

As far as Thailand is concerned, the manufacture of refractories from the high quality materials may require the addition of impurity to ensure adequate sintering at a comparatively low temperature. Iron oxide either as an ash from solid fuel or as cheap boiler scale is an effective additive in increasing sintering as measured by the bulk density (Table IV.VIII). It is commonly employed in European practice.

TABLE IV.VIII - BULK DENSITY OF FIRED DOLOMITE WITH IRON OXIDE ADDITIONS

Sample	Fired at 1600°C, 2 hours				Fired at 1800°C, 2 hrs. no addition
	no addition	1% Fe_2O_3	2% Fe_2O_3	3% Fe_2O_3	
KS	2.09	2.89	3.10	3.20	3.03
KMN	2.09	2.69	3.10	3.18	3.12
RKW	2.25	2.62	2.94	3.00	2.72
WW	2.31	2.93	3.13	3.36	3.00
WF	2.44	2.98	3.12	3.22	3.13

It may be concluded, therefore, that several deposits of dolomite in Thailand would be excellent for the manufacture of high grade refractory qualities and others for medium duty and as slag additions. Some of the formations are sufficiently pure to be used as a high grade precipitant of magnesia from sea water.

CHAPTER V

POTENTIAL USES OF DOLOMITE

For most of the industries which might use dolomite- e.g. aggregate, agriculture, glass-making -simple mining, crushing and grading of the mineral are all that is required to produce a suitable product. The refractories industry which embraces the production of sea-water magnesia and the manufacture of bricks, blocks and ramming mixes from dolomite involves much more complex technology and a raw material of precise characteristics.

Sea Water Magnesia

The average content of magnesium ions dissolved in sea water is about 1300 p.p.m. Simply by making the sea water sufficiently alkaline to a pH in excess of 10, causes magnesium hydroxide to precipitate virtually quantitatively. To achieve this condition, economically and industrially, involves the use of dolomite or other lime-containing mineral.

If dolomite is calcined at comparatively low temperatures it loses carbon dioxide and is converted into an intimate mixture of the oxides of magnesium and calcium. Careful rehydration of this calcine forms calcium hydroxide which is sufficiently soluble in water to produce the required alkalinity to precipitate magnesium hydroxide from sea water.

The chemical equations representing the reactions which occur are as follows:-

(i) $\underset{\text{dolomite}}{CaCO_3, MgCO_3} \xrightarrow[1200^\circ C]{} CaO + MgO$

(ii) $CaO + MgO + H_2O \longrightarrow \underset{\text{slightly soluble}}{Ca(OH)_2} + \underset{\text{insoluble}}{MgO}$

(iii) $Mg^{++} + Ca(OH)_2 + MgO \longrightarrow \underset{\text{insoluble}}{Mg(OH)_2 + MgO} + Ca^{++}$

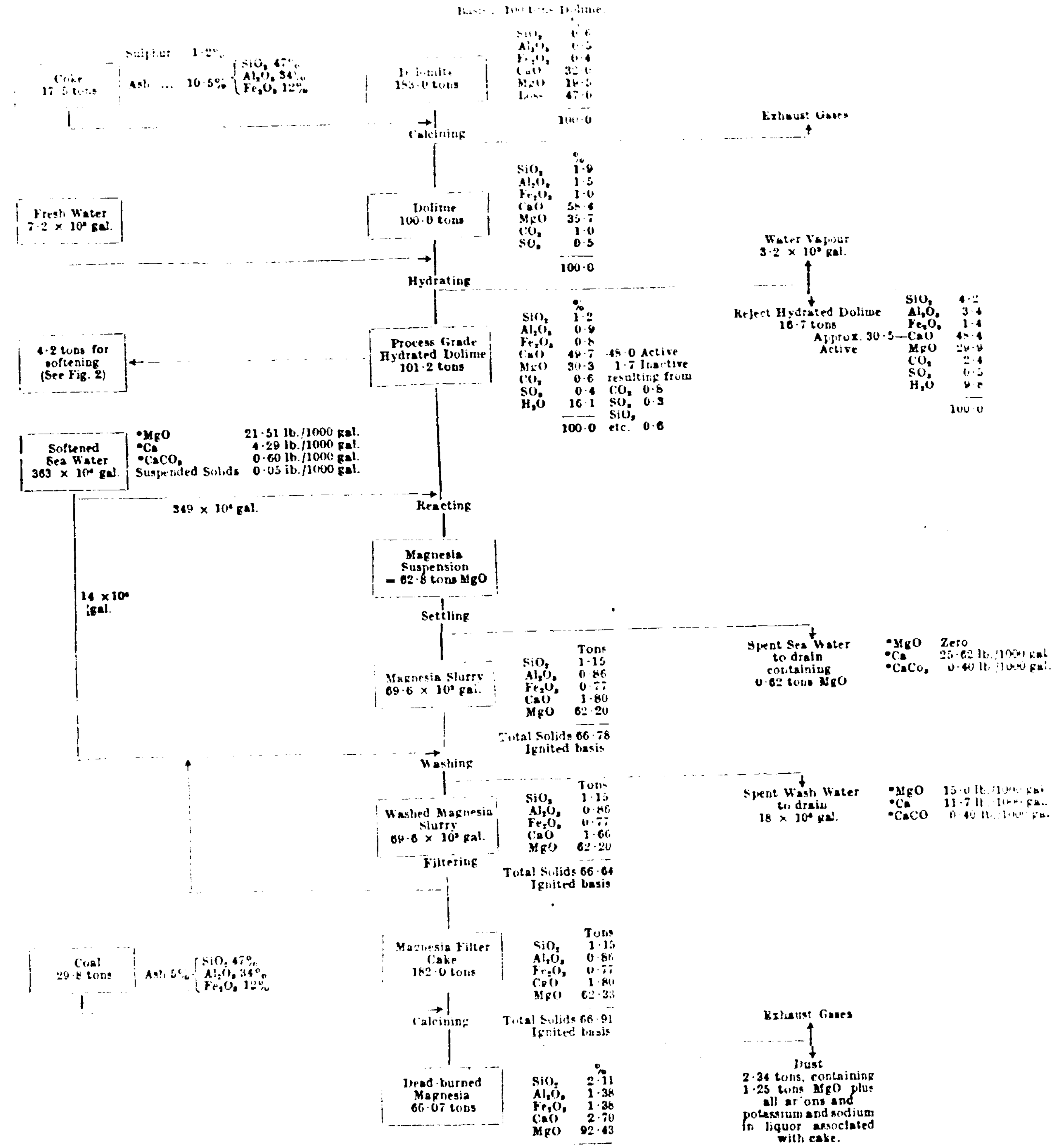
(iv) $Mg(OH)_2 + MgO \xrightarrow{+1700^\circ C} 2\ MgO\ \text{(periclase)}$

Approximately 3 tonne of pure raw dolomite are required to produce 1 tonne of magnesium oxide and this would involve treating 5×10^4 gallons (22.5×10^4 lts.) i.e. 225 tonnes of sea water.

The dolomite or other precipitant contains impurities - principally silica, alumina and iron oxide - and these tend to be insoluble and eventually contaminate the final precipitate of magnesium hydroxide and reduce the purity of the final calcined magnesia.

Gilpin has illustrated the process as operated at Hartlepool, U.K. (Fig. V.1) and from his figures a complete mass and chemical balance can be derived for any starting material.

Fig. V.1 : *Hartlepool Dolomite and Sea Water Magnesia Process Flow Sheet*



* Magnesium salts as MgO. Calcium salts as Ca. Carbon dioxide as $CaCO_3$

(after Thorp and Gilpin)

The lower the content of impurity in the dolomite, the purer will be the final product. So important is this factor, that the Steetley Co. Ltd. has had to change from dolomite to a pure limestone to obtain the high quality magnesia now required in high grade refractories. Thailand dolomites, particularly those from the Kanchanaburi/Pathuri areas are exceptionally pure and are equivalent to the purest limestone whilst still possessing the advantage of a high magnesium content which thereby increases the yield from the plant by a substantial amount.

Table V.I. compares the analysis of Thailand material with dolomites and limestones currently being used in the sea water magnesia process in the U.K.

TABLE V.I. - ANALYSIS OF CALCINED MATERIALS FOR SEA WATER MAGNESIA.

Sample		CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3
KS)	Range	59-60%	39-40%	0.2-0.7%	0.04%	0.08-0.5%
KMN)						
RKW)	Mean	59.4	39.2	0.42	0.04	0.26
Hartlepool dolomite		65-66	31-33	0.5	0.3-0.4	1.0
Hartlepool limestone		+99	0-1	0.2	0 - 0.1	<0.1

The analysis of the final product shown in Fig. V.I. contains a high proportion of lime as CaO. This is the result of co-precipitation or absorption of lime on the magnesium hydroxide which is much more prevalent when the sea water is cold. Sardaman (Sardinian magnesite) produced in the warmer Mediterranean Sea is appreciably lower in lime content.

So another requirement for sea water magnesia is an ocean near at hand which contains the normal proportion of magnesia in solution (circa 1300 ppm), is relatively free from suspended matter, has a rocky bottom, good circulating currents and ideally, is warm at all seasons.

The Gulf of Thailand has been surveyed and over 100 samples collected at various times of the year. Apart from the extreme north where rivers enter the Gulf, the salinity and magnesia contents are within acceptable limits. Table V.II summarises our results.

TABLE V.II - ANALYSIS OF THAILAND SEA WATER (PPM)

Mg^{++}	Ca^{++}	% Salinity	SiO_2	Fe_2O_3	B_2O_3	pH	Temperature °C Max	Min
1250-1450	400-470	31-34	7-10	0.08-0.30	7-12	8.0-8.2	31	26

These figures indicate that the chemical content and the temperatures in the sea water of most of the Gulf of Thailand would be ideally suited to the extraction of magnesia. The nature of the sea bottom is also important in that it should be rocky rather than sandy or silty; in conjunction with the Naval Department this aspect is being surveyed.

It is of interest that in tests on sea water brought to Leeds from the Gulf of Thailand and precipitated with Kanchanaburi dolomite calcined at 1100°C and then rehydrated, a product analysing to over 98% MgO (on a calcined basis) was produced. This would compare favourably with the best in the world.

World Production of Sea Water Magnesia

Over 90% of the world's requirements of magnesia for all purposes is now produced by precipitation from sea water or from brines or from bitterns.

Some authorities consider that there is over-production but, nevertheless, as Table V.III shows there are several new ventures in course of construction. Over the past few years there has been an increasing demand for high quality magnesia. This implies a high content of MgO (+ 97% MgO), low content of boron and a very dense product. Countries able to produce such a quality would

TABLE V.III : WORLD SEA WATER MAGNESIA PLANTS (1978)

1. Europe and the Mediterranean Area

Country	Location	D/b*	C/c**	Remarks
Seawater and brines				
Irish Republic				
Quigley Magnesite Co.	Dungarron	75 000	--	Subsid. of Pfizer Inc. of the USA
Israel				
Dead Sea Periclase	Arad	50,000	--	Owned by Israel Chemicals Ltd. and OEMAG
Italy				
Sardamag SpA	Sardinia	120,000	--	Expansion to 180,000 tpa in progress. Owned by Steetley, Didier-Werke, Casar, SANAC.
CO.GE.MA SpA	Sicily	65,000	--	Owned by SIRMA (itself part of FIAT)
Norway				
Norsk Hydro	Heroya	--	120,000	At present bulk used for Mg metal production
United Kingdom				
Steetley Refractories	Hartlepool	250,000		
USSR				
Sivash Works	Crimea	n.a.	n.a.	Capacity possibly as high as 100,000 tpa

Hungary -The Magnesite Company proposed 50,000 tpa plant producing magnesia from dolomite

New seawater MgO projects

Greece Scalistiri group proposed 100,000 tpa seawater magnesia plant at Euboea

Irish Republic -Cement Ltd. proposed 100,000 tpa seawater magnesia plant at Dhrogeda

Netherlands Billiton/Norsk Hydro -proposed 100,000 tpa magnesia-from-brines operation at Delfzijl

Yugoslavia -Magnobrom -proposed 100,000 tpa seawater magnesia plant in Montenegro

**D/b Dead-burned c/c caustic-calcined*

2. Asia and Oceania

Country	Location	D/b*	Remarks
Seawater magnesia			
China			
Manchurian Seawater Works	Liaoning	10,000	
Japan			
Ube Chemical Industries	Ube City	450,000	Owned by Ube Industries Ltd.
Shin-Nihon Chemical Industries	Minamata	198,000	Owned by Asahi Chemical Industry
Nihon Kaisui Kako	Nasetsu	50,000	Owned by Asahi Glass Co.
Asahi Glass Co.	Iho	15,000	

3. North America and Latin America

Country	Location	Capacity	Remarks
Seawater magnesia			
USA			
Barcroft Co.	Lewes, Del.	5,000	
Basic Magnesia Inc.	Port St. Joe, Fla.	100,000	Subsid. of Basic Inc.
Corhart Refractories Co.	Paxagoula, Miss.	40,000	Subsid. of Corning Glass
FMC Corp.	Chula Vista, Calif.	5,000	
A. P. Green Refractories	Freeport, Tex.	45,000	Magnesium hydroxide purchased from Dow Chemical
Harbison-Walker Refractories	Cape May, NJ	100,000	Subsid. of Dresser Industries
Kaiser Aluminum & Chemical	Moss Landing, Calif.	150,000	
Merck & Co. Inc.	South San Francisco, Calif.	15,000	Specified magnesia
Magnesia-from-brines			
USA			
Harbison-Walker Refractories	Ludington, Mich.	200,000	Magnesium hydroxide purchased from Dow Chemical
Martin Marietta Chemicals	Manistee, Mich.	250,000	Includes 80,000 tpa caustic-calcined capacity
	Midland, Mich.	65,000	
Michigan Chemical Corp.	St. Louis, Mich.	25,000	
Morton Chemical Co.	Manistee, Mich.	5,000	Specified magnesia
Seawater magnesia			
Mexico			
Quimica del Mar SA	Tampico	50,000	Subsid. of Industrias Penoles
Magnesia-from-brines			
Mexico			
Quimica del Rey SA	Laguna del Ray	34,000	Subsid. of Industrias Penoles

* D/b Dead burned ** C/c Caustic/calcined

find a ready export market which could be world-wide. The U.S.A., for example, supplies considerable quantities of high grade material to Europe.

Processing plants are usually designed to produce at least 100,000 tonnes MgO/annum but smaller units (50,000 tonnes/annum) are not uncommon and at the other end of the scale Japan has one installation capable of producing 500,000 tonnes/annum.

In late 1977, the processing plants listed in Table V.III were in operation. Not all of the operations use dolomite as a precipitant simply because this mineral in a sufficiently pure form is not common particularly near to suitable seaboards.

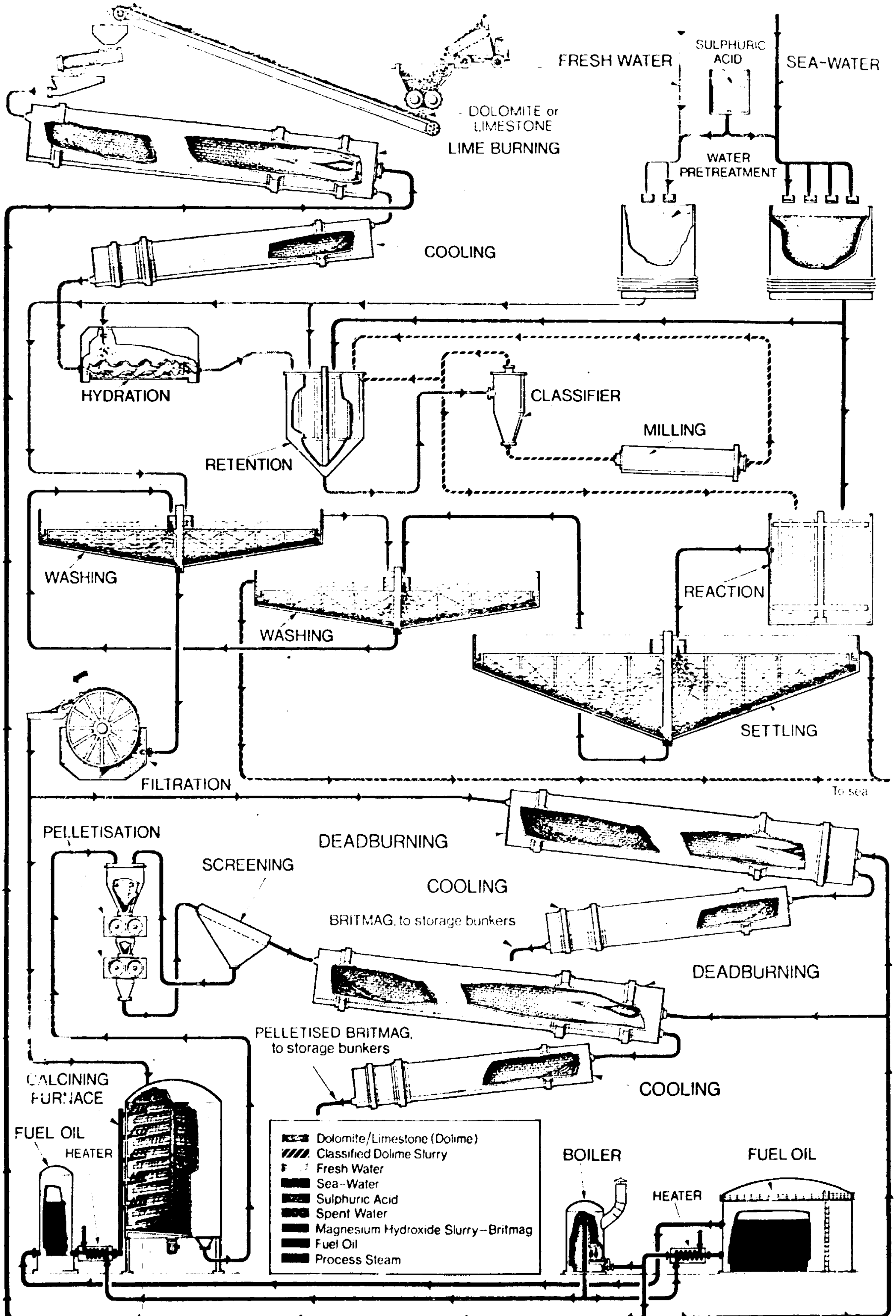
Plant Requirements- Fig. V.2 shows the complete schematic lay-out of the Steetley Hartlepool plant to produce refractory grade magnesia from sea water using dolomite as the precipitant. All other plants are based on the same principles.

A three part operation is required. Firstly, dolomite is lightly calcined (circa 1200°C) and then slaked. Secondly, sea water is pumped into huge concrete tanks after it has been mixed with a slurry of the slaked, calcined dolomite. Thirdly, precipitated magnesium hydroxide settling in the tanks is filtered and then calcined at high temperature (+1700°C) to produce a stable product for refractories. For chemical and agricultural uses, the high temperature calcination is not required.

If a fully integrated dolomite refractory and sea water magnesia plant were to be constructed in Thailand, one rotary kiln would probably be able to handle all calcining requirements:

a) high temperature treatment of dolomite at 1700°C.

b) low temperature calcination of dolomite for sea water precipitation at 1200°C and


FRESH WATER
SULPHURIC ACID
SEA-WATER
DOLOMITE or LIMESTONE
LIME BURNING
WATER PRETREATMENT
COOLING
HYDRATION
CLASSIFIER
MILLING
RETENTION
WASHING
REACTION
WASHING
SETTLING
FILTRATION
To sea
PELLETISATION
DEADBURNING
SCREENING
COOLING
BRITMAG, to storage bunkers
DEADBURNING
PELLETISED BRITMAG, to storage bunkers
COOLING
CALCINING FURNACE
FUEL OIL
HEATER
Dolomite/Limestone (Dolime)
Classified Dolime Slurry
Fresh Water
Sea-Water
Sulphuric Acid
Spent Water
Magnesium Hydroxide Slurry – Britmag
Fuel Oil
Process Steam
BOILER
FUEL OIL
HEATER

c) dehydration and calcination of magnesia product at + 1700°C

d) produce a slag addition quality of dolomite calcined at 1200-1350°C.

In this way a rotary kiln of economic size could be installed.

This rotary kiln would be the major cost and power item of the sea water plant. The main reactors involve civil engineering construction in concrete and other items include pumps, filters, conveyors, agglomeration units, sizing and bagging equipment.

For 100,000 tonnes of magnesia a year, capital cost, at present day prices, should not exceed £25 x 10^6 (1200 x 10^6 Bahts) and might be nearer £20 x 10^6 (1000 x 10^6) in Thailand.

Good quality crushed and graded magnesia commands £120 - 150/tonne in world markets and a profit margin would normally be sufficient to recover capital outlay in not more than five years.

There would be a feed back of magnesia to the refractories plant producing dolomite products which would increase its capacity and range of finished refractories.

Refractory Grade Dolomite

There are many qualities of dolomite refractories used in a wide range of high temperature industries such as iron and steel, cement, ceramics, glass-making, copper smelting etc. Although it is an excellent refractory, dolomite suffers from the problem that its lime component cannot be stabilised by heat alone and it will rapidly rehydrate on exposure to the atmosphere. This causes serious problems of cracking, dusting and eventually complete disintegration. Some means of protecting the lime has, therefore, to be found. The main groups of refractories based on dolomite are tar-bonded, ceramic-bonded, tar or pitch impregnated, stabilised qualities, chemically bonded bricks and blocks and ramming mixes. It is common practice to mix sintered magnesia and dolomite together to give an enriched product which is then manufactured in the various qualities listed below. The main manufacturing processes for refractories are as follows:-

1. Tar bonded. Carefully graded calcined dolomite is intimately mixed with 6-10% hot tar or pitch. The mixture is formed into shape under very high pressure up to 8t/in^2. The tar-coating reduces the rate of rehydration and subsequent disintegration and minimises dust formation during handling or storage; this process is called semistable because the products have a very short storage life but, nevertheless, provided precautions are taken and the bricks used quickly, they are an excellent refractory and relatively cheap.

2. Tempered Quality. The tar-bonded bricks are heated between 300-500°C to remove volatiles from the tar and induce some "graphitisation". These bricks are less subject to "fuming" in practice and are frequently preferred in steel furnaces.

3. Ceramic-Bonded. In this quality, dolomite which has been sintered at very high temperatures is crushed and carefully graded and then pressed into shape at 8-10t/in^2 with a non-aqueous liquid bond. The products are then refired in a tunnel kiln to a maximum temperature in the range 1350-1650°C, under which conditions, reactions occur which produce permanent ceramic bonding. Ceramically-bonded bricks are liable to rehydration so that storage for more than a few weeks (days in some cases) must be avoided, but their advantage is that they are "fume-free" in service.

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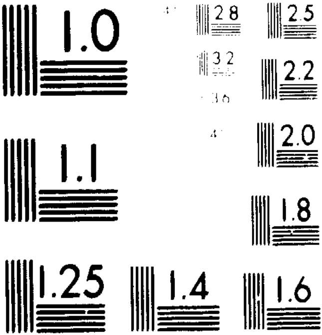

1.0
2.8
2.5
3.2
2.2
3.6
2.0
1.1
1.8
1.25
1.4
1.6

4. Tar or Pitch-impregnation. To improve final durability still further, the ceramic-bonded product, whilst still hot from the kiln, is dipped in a hot, very fluid bath of special tar or pitch. In some industrial practices this process can be carried out under vacuum.

The pitch penetrates and fills the pores of the bricks or blocks so that when the product is removed from the batch and colled there is almost complete saturation and protection of the dolomite by the organic bond which hardens on cooling.

Such dolomite products are much more resistant to rehydration and may be able to withstand several months of outside storage before serious deterioration occurs. This quality is acceptable for export and, indeed, tar-impregnated dolomite refractories from both the U.K. and West Germany have been imported successfully into Thailand in recent years.

In all tar-containing products the protective qualities of the organic additive are destroyed when they are heated under oxidising conditions in a furnace. Hence care has to be taken in any installation where dolomite refractories are used, not to allow cooling and exposure to the atmosphere to occur once the furnace has been burnt in.

5. A "Stable" dolomite brick was formerly manufactured by persuading the lime component to react with another ingredient to form a compound which was not subject to re-hydration and did not have other injurious qualities. The most successful venture was to induce the formation of tri-calcium silicate by intimately mixing a finely-divided

silica-containing/..

mineral with the calcined dolomite batch in carefully controlled proportions. The magnesium silicates, talc and/or serpentine were preferred in that these were naturally of small crystallite size and contributed some additional magnesia which improved the refractory quality.

Although such refractories had excellent potential, in theory, they were not able to live up to expectation because of the problems in securing the precise conditions of manufacture in terms of correct blending, intimate mixing and careful firing to ensure that the correct mineral phases developed.

As far as can be ascertained no "chemically-stabilised" dolomite refractories are now being made in Europe although they were quite popular up to about 1970.

6. Chemical bonding of dolomite refractories is being actively investigated by the research sections of most of the major producers. Their findings are a closely guarded secret but the aim is to stabilise the lime component either by increasing crystal growth or by modifying the lattice structure or by developing new crystal phases which are not subject to rehydration. Additives being investigated include iron oxides, boric and phosphoric acids, chromates, aluminates sometimes in conjunction with silicates.

Although the ultimate answer to dolomite stabilisation has not yet been found, the modern tar-treated shape, perhaps with chemical addition to increase sintering, is an excellent refractory possessing many advantages over alternative materials. In addition, it is much cheaper to produce than other basic refractories.

World Production of Dolomite Refractories

This aspect has been covered in Chapter III(p.40). It is sufficient here to emphasise that dolomite as a refractory is important when there are indigenous supplies of high quality mineral near to steel or cement producing areas and in countries where supplies of magnesia and high aluminas are not readily available at an economic price.

The greatest emphasis on dolomite has been in Western Europe with West Germany, France and the U.K. dominating the market and producing excellent qualities backed by advanced technology and science.

This situation could be mirrored in Thailand, where there are no local reserves of either magnesite or high alumina minerals, but large deposits of excellent dolomite which the present research has shown to have great potential in the manufacture of refractories.

Plant Requirements

The first essential step in producing good quality dolomite refractories is to manufacture an excellent calcine which must be of high chemical purity and extremely dense and well-sintered. This must then be carefully crushed, screened and a composite regraded to give the maximum packing density.

In dolomite technology, more so than in most other refractories, the principles of dense packing of composite materials must be rigidly observed by strict attention to blending and mixing.

The rock, as mined, has to be reduced in size in cone or impact crushers and fractions with a narrow size range (e.g. 5-20, 20-40, 40-100 mm) are screened for calcining in a rotary or shaft kiln to a temperature between 1600 - 2000°C. Dust is produced in the early stages of calcining and this has to be withdrawn.

The calcined product from the kiln is further crushed and screened into various fractions, accurate proportions of which are then reblended for the final refractory shapes.

At all stages, rejection has to occur and it is adviable that a multi-product plant is designed, of which only a minor proportion of the tonnage may be for refractories production.*

Fig. V.3 a, b, is a complete lay-out of a processing plant for dolomite. Inferior grades are screened into aggregate sizes after crushing; part of the product is diverted for agriculture or glass making and other qualities are acceptable for slag additions. Refractory block and brick production is from the best quality calcine which is correctly crushed, graded and reblended (Fig. V.3b). Any rejects are used as fettling grades.

This is a generalised plant embracing the essential features of the Wulfrath works in West Germany but it is similar to that of most other producers and it could form the basis of a manufacturing plant in Thailand.

It would be advisable to design a multi-purpose plant particularly for products from a rotary kiln which would be essential for the high quality dolomite from the Kanchanaburi area. The larger the size of a rotary kiln, the greater is its efficiency but the requirements of dolomite refractories within Thailand would justify only a small unit.

Small rotary kilns to produce sintered doloma at 1800°C at a rate of 10,000 t/year are available and might be justified economically in Thailand. A typical range of tar-bonded, ceramically-bonded and tar impregnated bricks and blocks and various ramming and patching compositions could then be manufactured. Alternatively shaft kilns or even tunnel kilns could be employed.

* The remaindor is used as slag additions or fettling grades.

FIG. V.3.a : PREPARATION PLANT

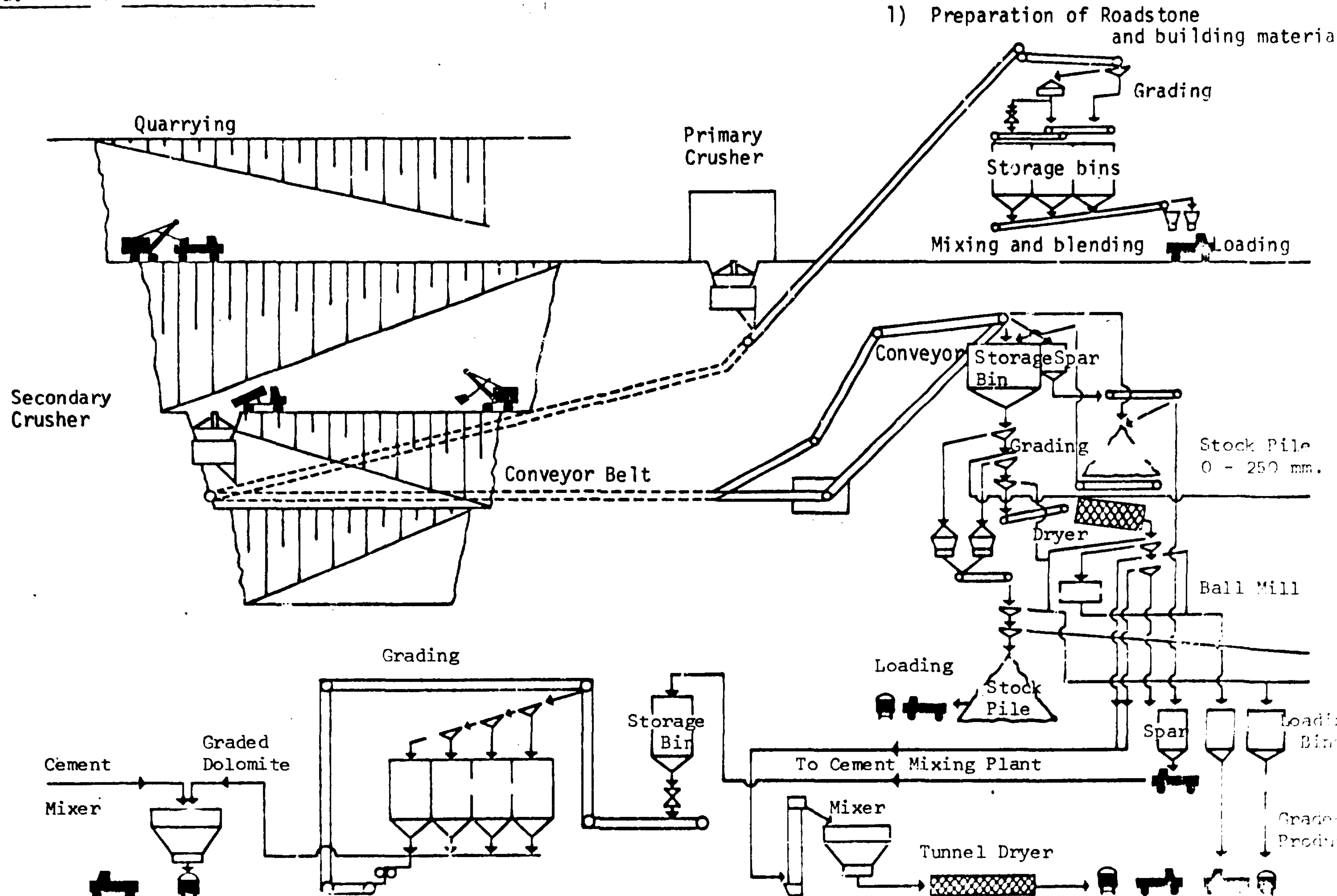
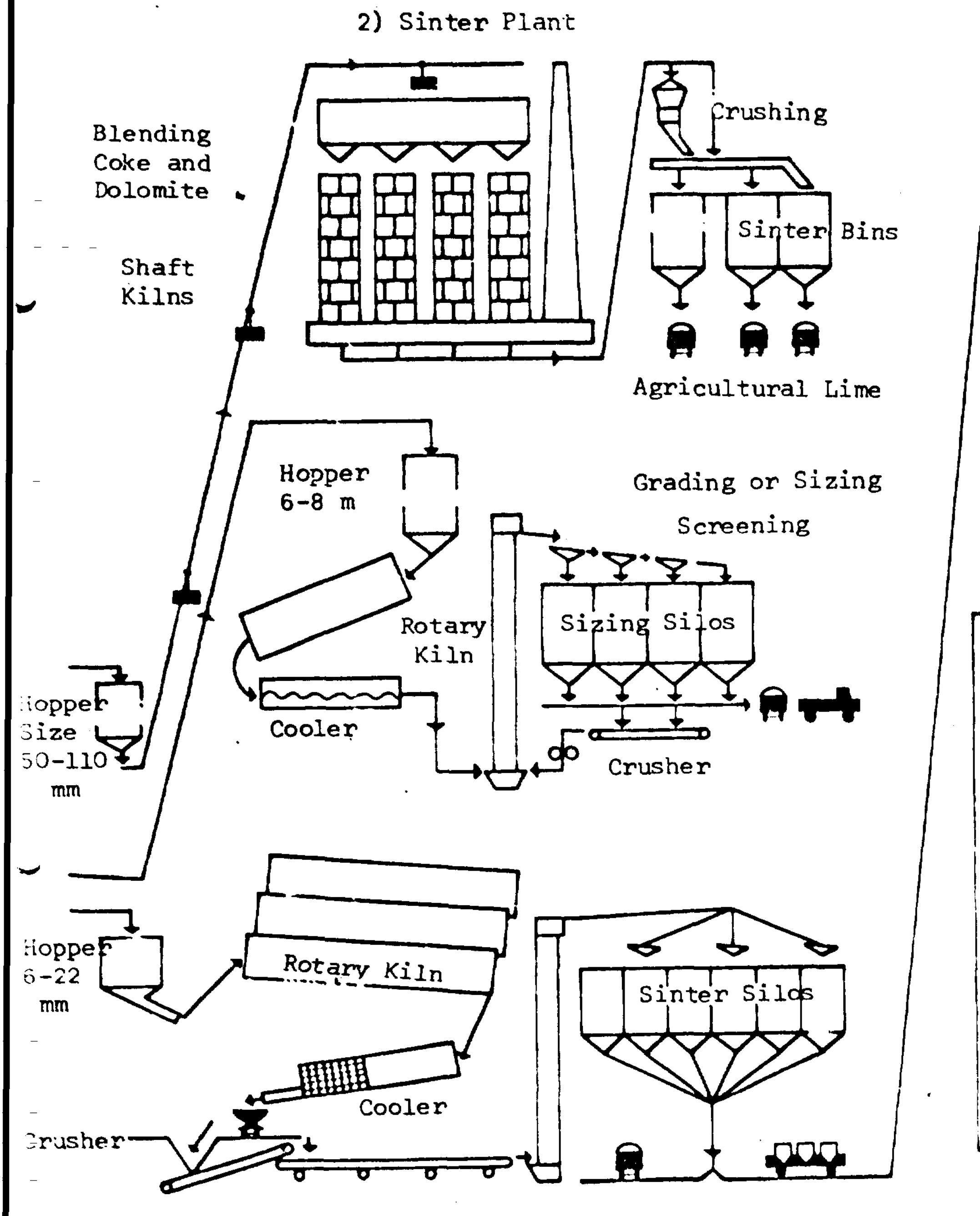
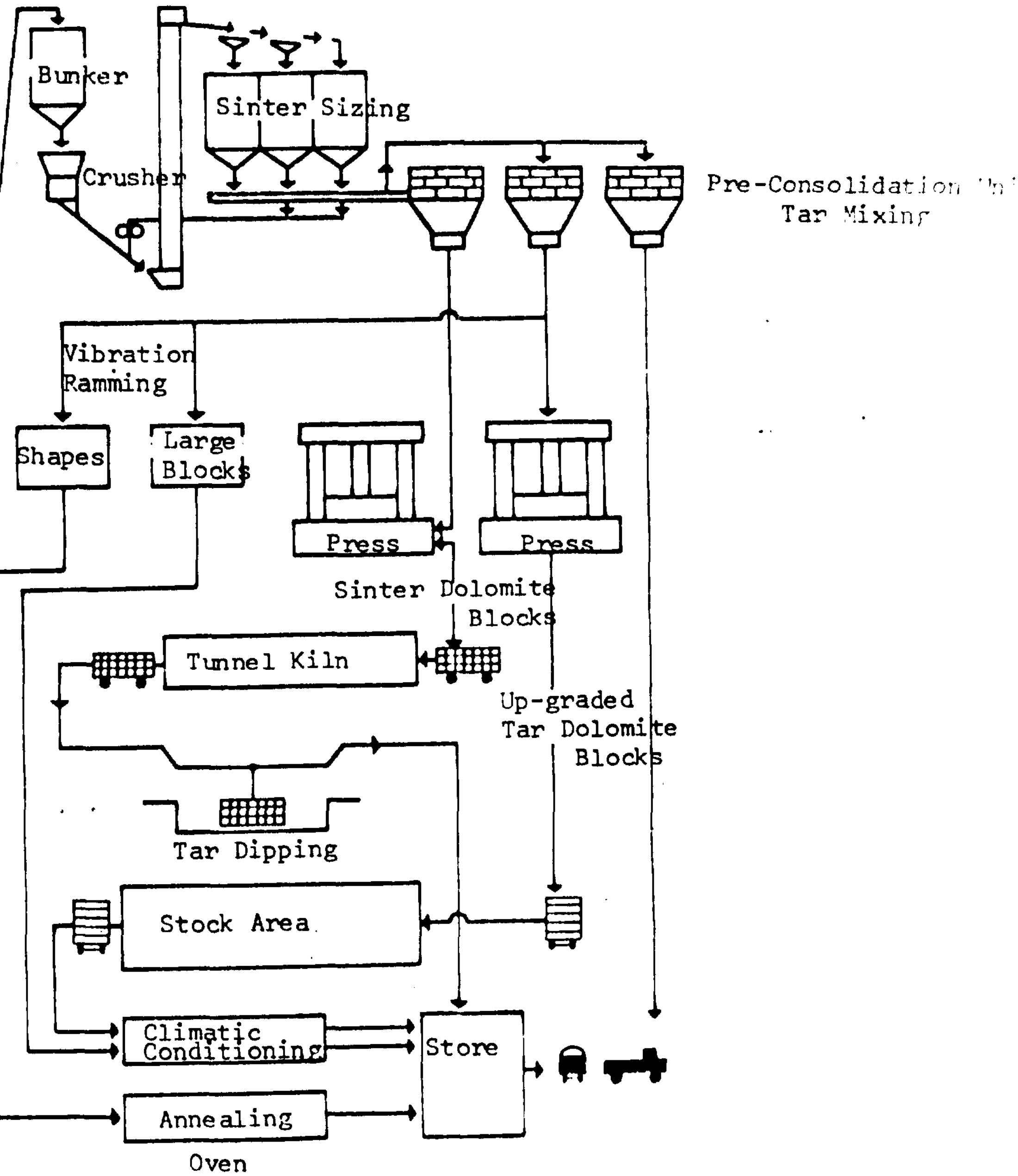


FIG. V.3.b: CALCINING PLANT



3) Block and Brick Making



It is calculated that for an annual production of 20,000 tonnes, capital costs would be of the order of £5 x 10^6 (280 x 10^6 Bahts) (August 1980). This would include a rotary kiln crushing, screening and grading facilities, mixing, pressing and full tar treatment. Production costs are not easy to predict without a more detailed knowledge of financial investment conditions, fuel charges and labour costs but in Western Europe an average figure of £140/tonne may be taken which includes all charges and full amortisation. The selling price is about £190/tonne.

Properties of Dolomite Refractories

With the assistance of Steetley (Refractories) Ltd., Worksop, U.K., full sized dolomite bricks have been prepared from Thailand raw materials under industrial conditions which would prevail in a large scale plant.

Samples from Kanchanaburi KMN and KS had been shipped in quantity for the trial.

The raw material was crushed and a sufficient quantity of size 5 mm to 20 mm was screened out for calcining in a pilot scale tunnel kiln to a temperature in excess of 1700°C.

The product was then further crushed and graded to the Steetley specification, mixed with non-aqueous additives and pressed into brick shape at 10 t/sq. in. These were refired in a tunnel kiln to 1600°C to produce a ceramically bonded product.

The bricks were of excellent shape and quality. Their properties have been compared with U.K. and German dolomites and the results presented in Table V.IV.

TABLE V.IV. : PROPERTIES OF DOLOMITE REFRACTORIES

Properties	Steetley U.K.	Steetley U.K.	Wulfrath Germany	Wulfrath Germany	Thailand KMN	Thailand KS
	Pitch Bonded	Ceramic Bonded	Pitch Bonded	Ceramic Bonded	Ceramic Bonded	Ceramic Bonded
Chemical Analysis %						
CaO	54.0-58.0	54.0-58.0	59.2	59.2	59.1	59.7
MgO	39.0-41.0	38.0-41.0	38.2	38.2	39.2	39.8
SiO_2	0.9- 1.4	0.9- 1.3	1.0	1.0	0.67	0.42
Al_2O_3	0.5- 0.8	0.3- 0.6	0.8	0.8	0.04	0.04
Fe_2O_3	1.5- 2.1	0.9- 1.3	0.8	0.8	0.08	0.15
Bulk Density g/cm^3	2.80-2.95	2.75- 2.90	2.85	2.85	2.82	2.80
Porosity %	-	16-20	14	16	18	18
Cold Crushing Strength N/mm^2			40	70	65	62
Compressive Strength N/mm^2 at 20^oC	21-42	25-60				
at 120^oC	5-21					
at 180^oC	4-14					
at 300^oC	2- 6					
Thermal Conductivity W/mK at mean 900^oC	2.4-2.9	2.5-3.0				
Carbon Retention after coking at 1000^oC wt %	1.5-1.9					
Loss on Ignition wt.%	3.4-4.2					
Permanent volume change % 5 hrs. at 1600^oC		-1.5 to -2.5				

This test confirmed that excellent dolomite refractories could be made from Thailand materials. There was insufficient quantity available to permit a large scale industrial trial in a steel plant furnace, but the laboratory tests are a sufficient indication that they would be of excellent characteristics although rather more prone to hydration - because of their greater purity - than their European counterparts. This could be mitigated if not eliminated by using a higher calcining temperature.

CHAPTER VI

FEASIBILITY OF DOLOMITE UTILISATION IN THAILAND

To be a feasible proposition, a production plant involving mining an ore body and then processing it into a suitable form for industrial use, must satisfy the following conditions:-

(i) the ore body must be available in sufficiently large quantities and it must be of consistent and adequate quality.

(ii) the industries which use the finished product must require it in sufficient quantity and at a price which will justify constructing and operating a plant.

(iii) as a consequence the capital costs and running costs of the mining and processing operation at the tonnage required must yield an economically attractive product.

(iv) The manufacturing unit must be sited in a position convenient for both raw material supplies and to the user industries and there must be ready access.

(v) Ancillary material supplies such as fuels, chemicals, water must be readily available.

(vi) The area chosen must have adequate services and a readily available work-force and skilled technical and managerial staff.

Raw Material Reserves

Thailand has many surface deposits of dolomites of excellent quality. The best, so far, examined in terms of purity are in Kanchanaburi/Ratburi areas; other districts not surveyed are likely to have good grades. There are other deposits of slightly inferior grade (Ko Si Chang) which could be used in many applications. Many individual formations are likely to yield in excess of 1×10^6 tonnes of consistently good dolomite.

Industrial Uses

The two industries which are established on a large scale in Thailand and which could use refractory materials based on or derived from dolomite are (i) iron and steel. (ii) cement. Only minor amounts could be envisaged in other areas but raw or lightly calcined dolomite would be needed in quantity in slag control, as an aggregate or in agriculture and there might be several outlets for magnesia if it were produced.

The feasibility and size of a potential dolomite industry must, therefore, be based on the demands for it in the two major consuming industries.

1. Steel. The philosophy of dolomite/magnesia utilisation has been developed in Chapter III and the conclusions apply also to Thailand.

   For the major melting and processing furnaces for steel, basic refractory linings are required. Strictly on the basis of quality and performance, magnesia-based refractories are preferred but where a country has a good resource of dolomite, refractories can be produced relatively cheaply from it and hence it can be widely used. Countries with no suitable dolomite, use predominantly magnesia.

   Thailand has good and plentiful supplies of dolomite but it could also develop magnesia from sea water. If the proportions of each were to mirror U.K. practice the ratio of magnesia:dolomite refractories would be 3-4:1. If magnesia were not produced indigenously and had to be imported, more dolomite could be utilised and the ratio would be 2.5-3:1.

   The steel industry will be developed along modern lines and so also will the cement industry, so that it can refractory products will be:-

Magnesia-based refractories	10,000 t per 1 x 10^6 of steel.
Dolomite-based refractories	3,000 t per 1 x 10^6 of steel.
Dolomite-based refractories	1,000 t per 1 x 10^6 of cement.

In addition, for slag control in the major converters, 25-30 Kg/tonne steel of lightly calcined raw dolomite would be utilised. Fettling grades of sintered dolomite would also be needed up to 3 Kg/t steel.

Steel Production in Thailand and the ASEAN Community.

The feasibility of manufacturing dolomite refractories or establishing a sea water magnesia plant in Thailand depends to a large extent on an accurate prediction of the production of primary steel and steel products and on export potential to other ASEAN countries for use in their steel industry. These issues involve many imponderables and depend on decisions which are political rather than technological.

Every ASEAN country has a well-established steel industry but with capacities which greatly exceed production. At present steel consumption is much larger than actual production because there are considerable imports of ingots and of finished steel products mainly from Japan. It is a consequence of the present world recession that imported steel products into Thailand are frequently cheaper than the equivalent article processed by the local industry. It is not easy to forecast when and if the situation will change.

Dr. Kasem Balajiva of ASRCT in 1975 predicted that the growth rate in steel consumption in Thailand would be about 10%/annum and if his calculation should prove correct it would reach at least 2.5 x 10^6 tonnes by 1985 and 7.3 x 10^6 tonnes by the year 2000. These figures are not unreasonable when viewed in the context of the proposed developments in the country. The only problem is in predicting the proportion which will be home produced and that which will be imported.

The steel industries of Thailand and other ASEAN countries use steel scrap as a raw material about 50% of which is imported. Most of this is melted in electric arc furnaces to produce ingots and billets. Accurate figures are notoriously difficult to obtain but it may be hazarded that the steel consumption figure of 1.57×10^6 tonnes in 1978 for Thailand was made up of:

500,000 primary smelting and refining

630,000 reprocessed scrap (electric arc furnaces mainly)

440,000 imported finished products.

This situation must change within the next few years because scrap steel supplies will be drastically reduced and there are firm proposals for the Thai steel industry to become independent of imported sources of steel. In 1979, an Austrian pre-feasibility study proposed a 400,000 tonne/year sponge iron plant and Mannesmann Demag A.G. of West Germany is collaborating with Thailand rolling mill operators in a proposal for a completely integrated steel mill of 1.2×10^6 t/year capacity. Iron ore would be imported and natural gas from off-shore fields would provide the main fuel.

Whether these schemes come to fruition or not, the steel industry of Thailand is expected to require between 16,000-33,000 tons of basic refractories in 1985 of which about one-third could be dolomite; these figures would rise to $47-95 \times 10^3$ tonnes by 2000 ($15-32 \times 10^3$ tonnes dolomite). Within the ASEAN community, over five times these tonnages would be required.

At present all basic refractories are imported into Thailand, either in the form of finished bricks, blocks or ramming mixes or as fully sintered grains to be manufactured into shapes locally; all are magnesia-based. In 1979 about 9,000 tonnes of magnesia refractories were imported for the steel industry alone at an estimated total cost of over 150 x 10^5 Bahts (£3.5 x 10^5).

Cement Industry in Thailand

Thailand is an important producer of cement in the Far East with an annual production (1979) in excess of 4 x 10^6 tonnes. There are plans to increase and it is confidently predicted that by 1985 over 8 x 10^5 tonnes will be manufactured.

So successful has dolomite been in cement kilns, both economically and technologically, that if refractories from it were produced in Thailand, it would be an automatic choice as a lining material in preference to the present expensive imported magnesia and high aluminas.

By 1985, therefore, dolomite refractory consumption in cement kilns is likely to be 8,000 tonnes/annum.

Viability of Refractory Production

Taking the two major u[illegible]r industries together, therefore, the total demand for dolomite refractories in Thailand in 1985 should be between 14-20 x 10^3 tonnes rising to 20-46 x 10^3 tonnes by the turn of the century.

The demand for magnesia as a refractory for the steel industry, on the same basis of calculation, will be in the range 11-22 x 10^3 tonnes in 1985 rising to 31-63 x 10^3 tonnes in 2000 (assuming all cement kilns use dolomite).

If agreement could be reached within the ASEAN community for Thailand to supply all the dolomite refractories and magnesia which are required for the steel and cement industries the following predictions could be made:

TABLE VI.1. : HYPOTHETICAL USAGE OF BASIC REFRACTORIES IN ASEAN COMMUNITY 1985 - 2000

Year	Dolomite Refractories	Calcined Seawater magnesia
1985	40,000 tonnes (averaged)	75,000 tonnes (averaged)
2000	[illegible]4,000 " (averaged)	210,000 " (averaged)

From the figures derived in the previous section, and based solely on Thailand's needs, 14-20 x 10^3 tonnes of dolomite refractory will be required by 1985. Taking into account the loss of carbon dioxide and fine materials (which can be used for other purposes) the raw stone to kiln will be 45-60 x 10^3 tonnes i.e. 130-170 tonnes/day in 1985. By 2000 it will have risen to a minimum of 250 tonnes/day.

If agreement within the ASEAN nations for the supply of dolomite refractories is assured, a manufacturing plant based on rotary kiln firing would be completely viable.

Even if there were no certainty of export, a dolomite refractories plant using high grade raw material would be a necessity if only to reduce the high cost of imported basic refractories. Rotary kiln firing would be the best technique to produce a high density sintered product even though this would be a small, relatively high cost unit. Some shaft kilns perform well in small quantity manufacture and are much less costly but their product is less uniform.

Correctly designed, a refractories plant can be constructed so that additional streams can be introduced as demand increases but sintering kilns are the major cost item.

Viability of Sea Water Magnesia Production

Although small units have been constructed to meet requirements in specialised areas, it is considered uneconomical to build sea water magnesia plants with a capacity of less than 50,000 tonnes/annum, and 100,000 tonnes/annum capacity and upwards are nowadays preferred.

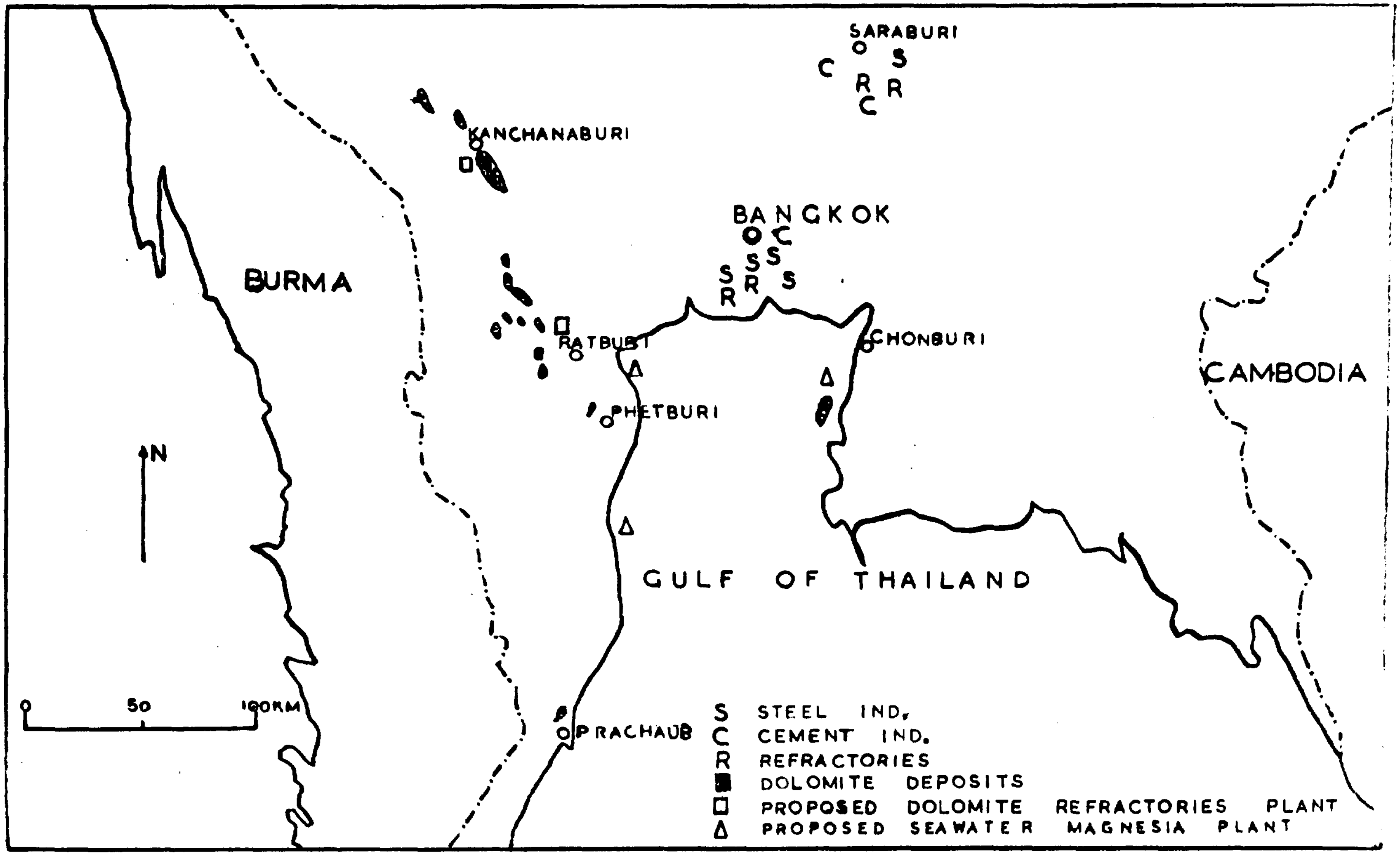
On this basis, a plant to manufacture for Thailand's needs alone could not be justified even on a year 2000 projection. If it were supplying all ASEAN countries there would be justification but unlike dolomite refractories, magnesia of high quality is manufactured elsewhere in the Far East in large economical units. There would be intense cometition.

In favour of a Thailand venture would be potentially a very pure product and one which should be cheaper than Japanese and other Far East producers in that good dolomite is available as a precipitant whereas most other producers have to use calcite.

This aspect of our research programme would require more detailed economic study and decisions at top level within the ASEAN Community, but with the present information we could not recommend the establishment of a conventional sea water magnesia plant at present.

However, a significantly important advantage may accrue if dolomite activities were centred on Ratburi. On the coast road to Bangkok and not more than 30 Km from the dolomite outcrops, there is a large solar - or sea salt activity. The bitterns from this process are enriched in magnesia so much so, that a much smaller unit with a consequently lower capital outlay and running costs can produce substantial amounts of magnesia by the dolomite precipitation route. This process is in operation in Mexico and Israel. Furthermore, production units to manufacture as little as 10,000 tonnes/annum of magnesia are economically and technologically feasible. The calcining and dead-burning of the magnesia can be completed in a shaft or tunnel kiln operating at +1700°C. This would be an extremely attractive venture and should be investigated further. In 1976 252,000 tonnes of bittern containing an estimated 16,000 tonnes MgO equivalent was discarded.

FIG. VI.1 : LOCATION OF EXISTING STEEL AND CEMENT WORKS IN THAILAND AND POTENTIAL DOLOMITE AREAS.



Logistics of Potential Processing Plants

The attractiveness of the high quality dolomite around Kanchanaburi/Ratburi in comparison with other formations so far examined makesthis the ideal area for processing plants to be established. The area is also favourably placed with regard to the major user industries as is illustrated in Fig. VI.I.

If a sea water magnesia plant were to prove viable ultimately, it could be positioned on the coast between Petchburi and Prachuap and the calcined dolomite transported by rail.

Transport to Bangkok and the other industrial centres from Ratburi is by good fast roads.

There is a good fresh water supply and the area has a substantial population with some industry already established.

The fuel to be used in the processes of calcining and sintering needs careful thought. The alternatives would be lignite from the Lamphun area of Thailand, imported Australian coal, imported oil or natural gas from the Gulf of Thailand.

Some lignites in northern Thailand are low in ash and sulphur, that from Li is reported to contain 3.7% ash and 0.6% sulphur, but at present these are expensive, and not yet fully developed. In the pulverised fuel supplies demanded in Western Europe,3% ash is considered the maximum. Probably Australian coal implemented with natural gas will be the most satisfactory and economical compromise, but much will depend on the successful development of the off-shore areas.

The present plan is to bring the natural gas ashore on the eastern coast of the Gulf of Thailand and hence to the Bangkok area. It may not be extended to Ratburi for some considerable time. However, a new oil terminal and port installation is proposed for an area around Petchburi which would thus favour Ratburi as the best site.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The research programme has established the following facts:-

1) There are many extensive surface deposits of dolomite in Thailand, some of which, particularly in the area of Kanchanaburi/Ratburi are exceptionally pure when compared with other world resources.

2) These dolomites can be calcined satisfactorily and although a high temperature is required they can be sintered to a dense, hard mass suitable for manufacturing refractory qualities. Bricks and shapes have been manufactured from them which have proved to be equivalent in property to the best European products.

3) The waters of the Gulf of Thailand are warm, in many places free from impurities, and with average amounts of magnesium ions in solution. This can be precipitated with good-grade calcined dolomite to produce a high grade magnesia. A + 98% MgO has been produced under laboratory conditions from sea water from the Gulf and calcined Kanchanaburi dolomite. The yield was 97.4%.

4) A similar process could be used to extract magnesia from the bitterns of the sea salt process which is close to the dolomite formations. This could yield up to 16,000 t of high grade MgO/year.

5) The European and World refractories industries have been surveyed. It is concluded that all steel industry requires an average 13 Kg of basic refractories per tonne of steel of which dolomite, if it is available in good qualities, constitutes one-third; the rest is magnesia-based. Cement kilns require 1 Kg basic refractory/tonne of cement for which dolomite

bricks are well-suited.

6) On this basis Thailand industry will require:-

	Dolomite Refractories	Sea Water Magnesia
1985	14 - 20 x ^{3} t/a	11 - 22 x 10^3 t/a
2000	28 - 46 x ^{3}	31 - 63 x 10^3

7) If agreement can be reached within the ASEAN Community for Thailand to become the supplier of basic refractories these figures could be increased five times. There is also a possibility of exporting high grade basic refractories to other countries of the Far East.

Our recommendations are:-

i) T.I.S.T.R. should collaborate with the Thailand iron and steel industry with the intention of establishing immediately a dolomite refractories plant with an initial output of bricks and blocks of 20,000 t/year. This will be based on Kanchanaburi or Ratburi ore and will produce additional lower grade quarry material for aggregate, low fired dolomite for slag additive (about 200,000 t/annum) and 10,000 t/year of fettling grade calcined dolomite fired to about 1700°C.

ii) We are advising against pursuing a sea water magnesia operation at this stage on economic grounds alone even though the operation would be technically viable.

iii) There should be discussions arranged within the ASEAN Community concerning the potential requirements of calcined dolomite, magnesia and refractories made from them to formulate both a short and long term plan for the industry in Thailand. A working party possibly under the aegis of UNIDO experts should be established for this purpose.

iv) More detailed study is required of the bittern resources in Thailand and a feasibility exercise initiated to assess their potential in the production of the quantities of refractory grade magnesia required for local use - UNIDO support is recommended.

v) The Department of Mineral Resources (D.M.R.) should be requested to carry out an intensive survey of dolomite occurrences in the Kanchanaburi, Ratburi and Petchburi areas to quantify the dolomite resources and perhaps indicate even more suitable formations for development than we have been able to examine.

vi) T.I.S.T.R. should communicate these findings to the Steetley Co. Ltd., Workson, U.K. and seek advice on all technical, design and economic aspects raised in the proposed new projects. This company has given invaluable assistance in the research programme and will be willing to consider licensing their unrivalled "know-how" on both dolomite refractories and sea water magnesia. The company may also be interested in holding equity in any new venture and assisting with export schemes.

vii) The award to Mrs. L. Chotimongkol who conducted the research programme should be extended immediately for a further twelve months. This would enable her:

a) to continue her investigations and research into fundamental aspects of Thailand dolomite at Leeds University and so acquire a Higher Degree and professional qualifications.

b) to visit and discuss in detail, the operations of manufacturing dolomite and other basic refractories throughout Europe. Largely at her own expense she has collected material from Germany, Luxembourg, Belgium, France and the U.K. and gained valuable contacts but a longer period of experience in production methods is essential. She would need to study all aspects of design and operation of new plants in Thailand.

c) to visit Israel and/or Mexico where magnesia-recovery plants from bitterns and brines are in operation at tonnages similar in size to the proposed operation in Thailand.

The sum required will be £8,000 to include the following items:-

		£
i)	Additional University fees and costs	2,300
ii)	Accommodation and living expenses	2,800
iii)	Travelling Expenses and European visits	2,200
iv)	Visit to Israel or Mexico	700
		£8,000

Dr. Rex W. Grimshaw
Senior Lecturer, Leeds University.

Mrs. Ladawal Chotimongkol,
Research Officer, T.I.S.T.R.

APPENDIX

Additional work to contract 77/112/DR agreed 29.10.79.

i) Directory of Producers.

This has been dealt with in Chapter III which was extended to include a detailed description of a private visit to European centres of production.

For completeness the full list is as follows:-

EUROPE

BELGIUM

Carrières et Fours à Dolomie de la Sambre (SA)- Carsambre

Produits Dolomitiques de Merlemont SA (main producer)

Dolomie de Marche-les-Dames SA

Dolomie de Sambre et Meuse SA

Saint-Antoines Carrières SA

SA de Marche-les-Dames

(all the above, quarry and/or mine dolomite and crush and grade mostly for export).

EIRE

Quigley Magnesite Division of Pfizer Chemical Corporation,

Bennettsbridge, Co. Kilkenny.

(dolomite for sea water magnesia production)

FRANCE

Magnésie et Dolomie de France SA., Pas-de-Calais

La Dolomie Francaise, Neau, Mayenne and elsewhere

(main producer of France)

Blancs Minéraux de Paris SA, Aude

Denain-Anzin-Minéraux SA, Pyrénées

La Magnésienne and Soler Réunies, Hérault

Randon SNC, Pas-de-Calais

Sopromine SA, Aude

Samin, Lozère

GREECE

Fimisco, part of Scalistiri Group, Cadinsos, Euboea
(sea water magnesia and refractories)

ITALY

Dolomite di Montignoso SpA, Massa
Dolomite di Sestri SpA, Genova, Sestri-Ponente
Sanac, Massa (bricks)
Dolomite Franchi SpA, Marone
Società Dolomite Italiana SpA, Gardone Val Trompia
Mineraria Valtellinese SpA, Postalesio
Fabbriche Italiano Magnesia (Collotta-CIS and Figli), Molina

LUXEMBOURG

Refralux SARL, Luxembourg

NORWAY

A/S Norwegian Talc, Hammerfall (magnesium metal)
Franzefoss Bruk, Ballangen

SPAIN

Productos Dolomiticos SA, Santander (refractories)
Dolomitas del Norte SA, Oviedo
Steetley Española SA, Santoña
Iberdol SA, Motril (glass quality)
Roca Dolomitica SA, Coin

SWEDEN

Strabrucken AB, Sala (refractories)
Dyrkatorps Dolomitbrudd (sintered qualities)
Ernström Mineral AB, Glanshammer

TURKEY

Fertiliser Industry Corp., Kutahya

UNITED KINGDOM

Steetley Co. Ltd., Worksop (complete range) - many works

Raisby Quarries Ltd., Coxhoe (burned qualities)

Tarmac Roadstone Ltd., (aggregate)

Lockwood, Blagden & Crawshaw Ltd., Doncaster

Man-Abell Ltd., Coleford (aggregates)

G. R. Stein Ltd., Worksop (refractories)

WEST GERMANY

Dolomitwerke GmbH Wulfrath (refractories, agriculture etc. 90% German products)

Gersheimer Steine und Erden GmbH, Gersheim

Marmorkalkwerk Troesch KG, Holenbrunn

Kalk-und Dolomit-Werk GmbH, Aachen

Dolomitkalkwerk Anton Linneborn, Fretter

Stahl'sche Dolomit-und Kalk-Werke GmbH, Rupprechstegen

Klockner Durilit GmbH, Salzhemmendorf

Dolomitwerk Salzhemmendorf GmbH, Salzhemmendorf

Grevenbrucker Kalkwerke GmbH, Lennestadt

Trierer Kalk Dolomit-und-Zementwerke GmbH, Wasserbillig

Dolomit hartsteinwerk Wasserbillig GmbH, Wasserbillig

Harzer Dolomitwerke GmbH Wulfrath, Scharzfeld

NORTH AMERICA

U.S.A.

Basic Inc., Maple Grove, Ohio (raw and refractories) (main U.S.A. Producer)

Ohio Lime Co. (General Refractories Co.) Woodville, Ohio (raw and refractories)

Pfizer Inc., Gibsonburg, Ohio (mainly fertiliser)

Kaiser Aluminum and Chemical Corp., Natividad, Cal. (all grades, principally for sea water magnesia plant at Moss Landing)

Dolomite Brick Corp. of America, York, Pa. (bricks)

L. P. Green Refractories Co., Michigan (bricks, fettling quality)

CANADA

Steetley Industries Ltd., Hamilton, Ont. (mining, calcining, bricks)

Chromasco Corp., Haley (magnesium metal)

Sydney Steel Corp., Nova Scotia (bricks)

Mosher Limestone Co. Ltd., Nova Scotia (mainly agriculture)

Dresser Industries Canada Ltd., (raw and calcined)

MEXICO

Dolomita de Monclova SA., Ciudad de Monclova (raw)

Fundos Dolomita SA, Ciudad de Monclova (raw)

Cia Refractarios Fasicos, (bricks)

Quimica del Rey SA, (magnesia from brines)

Other important countries which produce dolomite for purposes besides aggregate and agriculture include Australia, Brazil, India, Japan, Pakistan, S. Africa.

2) Directory of Users and Applications

It would be impossible to produce a list of all users of dolomite except by setting down all steel plants in Europe, U.S.A., Japan and elsewhere and most of the cement works of Europe.

In Chapter V, a comprehensive description of all applications of dolomite has been included which is important for the narrative of the main report.

3) R and D Organisations and Universities Working on Dolomites

Apart from the major European producers of dolomite refractories there is surprisingly little research being carried out on dolomite in any part of the world. The main reason is that manufacturing companies have, themselves, large R & D departments and prefer to keep their work secret.

There is also much collaborative work between steel companies (users of dolomite) and producers; not much of this work is published in open journals. Because of our contacts with Steetley Co. Ltd., and the British Steel Corporation and with Wulfrath and the German steel industry we have been able to quote from private communications and produce facts which would not otherwise be available..

a) Steetley Co. Ltd., U.K. have research and development facilities into dolomite at all their divisions. Central R & D was abandoned about three years ago.

i) Hartlepool laboratories are constantly seeking to improve sea water magnesia production.

ii) Minerals Division, Carlton Hill, Worksop, is concerned with new deposits of dolomite both in U.K. and throughout the World.

iii) Refractories Division, Worksop, has R & D facilities in brick manufacture and use of dolomite in steel industry.

The Steetley Organisation sponsor work on dolomite at the British Ceramic Research Association Laboratories, Penkhurst, Stoke-on-Trent. This is mainly on property assessment. Also at University of Sheffield, on low temperature firing properties. There are training programmes for R & D personnel at University of Leeds and elsewhere. GR-Stein at Sheffield also have R & D sections working on dolomite.

b) Dolomitwerke GmbH, Wulfrath, at Hagen/Halden, West Germany has large facilities for R & D but confine their activities to Germany, Luxembourg, Belgium materials and provide a service to producers in these countries. There is a dossier on dolomites from all over the world.

The R & D department at Wulfrath is intimately linked with the German steel industry particularly as the refractories company is a subsidiary of August-Thyssen Hutte A.G., and Hoesch Werke A.G. which are its major customers.

There is no other research being undertaken outside the industry in Germany, but there are training programmes at Universities.

c) Dolomie Francaise have extensive R & D facilities at Neau (Mayenne) which are linked to the main dolomite brick producer at Flaumont (Nord) La Compagnie des Réfractaires Basiques and in turn to major French steel works.

4) Roster of Experts in Dolomite

This is difficult to compile. Many people are experts in one aspect of dolomite science or technology, such as mining, beneficiation, brick making, utilisation, sea water magnesia, but only a few have a wide experience. Virtually all of these complete experts are attached to a major company and I can only refer to them.

Dr. W.C. Gilpin) Mr. B. Bown)	Steetley Chemicals Co. Ltd., Hartlepool, U.K. (dolomite for sea water magnesia)
Mr. D. Clarke)	
Mr. E. Parry	Steetley Minerals Co. Ltd., Worksop (dolomite raw materials)
Dr. D.R.F. Spencer) Dr. M. Peatfield)	Steetley Refractories Co. Ltd., Worksop (dolomite refractories)
Mr. G. Plant	Steetley Minerals Co. Ltd., Worksop (expert on plant design, construction, costings etc.)
Dr. J. Laming	GR-Stein Co. Ltd., Worksop (dolomite bricks)
Mr. J.C. Drum) Mr. S. Tangney)	Cement Ltd., Ireland (dolomite for sea water magnesia)
Dr. W. Munchberg Technical Director	Dolomitwerke Wulfrath, West Germany.
Artelt P	Verein Deutscher Eisenhuttenleute, W. Germany.
Kronert W	Institut fur Gesteinshuttenkunde, W. Germany.
Konopicky K	Deutches Kieramik, W. Germany.

Berthoumieux G	Bureau de Recherches Geologiques et Minieres, Orleans, France
Vergerio J.M.	Compagnie des Refractaires Basiques, Paris.
Allard G.	La Dolomie Francaise, Neau, Flaumont, France.
Kraner H.M.	Kaiser Alumimum Co. Ltd., Berkeley, Calif. USA.
Zhukov A.V.	U.S.S.R.
Aliprandi C.	Italy.

5) List of References and Publications.

These have been divided into the Chapter headings of the main report.

CHAPTER II

Brown G.F. et al — Geological Reconnaissance of the Mineral Deposits of Thailand. U.S. Geol. Survey 1951. and Bull, Roy. Dept. Mines Mem. I. 1953.

Kabayashi — Geology & Paleontology of S.E. Asia. Univ. of Tokyo Press 1964.

Buravas S — Stratigraphy of Thailand Proc. 9th Pac. Sci. Congress, Bangkok 12 1957.

Alexander JB et al — Basement Rocks of Malaya. Amer. Sci., 5, 250, 1951.

Bunopas S. — Stratigraphic Successions in Thailand. J. Geol. Soc. Thailand 2, 31, 1976.

Tennant C.B. & Berger R.W. — X-Ray Analysis for Calcite & Dolomite. Amer. Min. 42, 23, 1957.

Krauskopf K. B. — Introduction to Geochemistry, McGraw-Hill 1967.

Warne S. St. J. — Staining Scheme for Carbonate Minerals J. Sed. Petr. 32 (1) 29, 1962.

CHAPTER III

Anon. Industrial Minerals — Dolomite 1 The Producers p.25, February 1976.

Anon. Industrial Minerals — Dolomite 2 Consuming Industries, March 1976.

Coath J.A. & Wilshire B. — Creep Properties of Doloma. Ceramurgia 4 (2) 66, 1978.

Staron J. — Firing Temperature on the Development of Basic Refractories. Bull. Soc. Fr. Ceram. 119,13, 1978.

	The Refractories Industry of Germany. Bul. Soc. Esp. Ceram. Vidrio 18 (3) 161, 1978.
Spencer D.R.F.	Refractories in the Eighties. Refract. J. 12, March 1979.
Gilpin W.C. and Gilbert F.C.	Industrial Minerals Metal. Bull. 173, 1975.
Bauer G.	Modern Ladle Line Practice in Germany. Sprechsaal 111, (4), 202, 1978.
Soc. Belge des Produits Refractaires	Process for Production of Doloma. Br. Pat. 1, 423, 910, 1976.
Thorp H.W. & Gilpin WC	Sea Water Magnesia Process. SCI(Chem.Eng.Gr.) 31, 1949.
Gilpin W.C. and Spencer D.R.F.	Development in dead-burnt Dolomite. Refract. J. n. 3, April 1972.
Schlegel E and Greiner R.	Production of Refractory Bricks from Sintered Lime. Silikattechnik 26 (8) 276, 1975.
Shumilin A.A. et al	Calcining Tkvartchel Dolomite in Rotary Kilns. <u>Refractories</u> (Russia) 34(10) 609, 1969.
Bron V.A. et al	Dolomite of the Lisegorsk Deposits. <u>Refractories</u> 17 (8), 474, 1976.
Dowsing R.J.	Materials from the Sea (Magnesia) Metals & Materials <u>20</u> Jan. 1978.
Kozhevnikov E.K. et al	Beneficiation of Dolomite, Ogneupory <u>3</u> 19, 1973.

<u>CHAPTER IV</u>

U.K. Refractories Committee	Tentative Methods of Testing Basic Refractories, Special Publ. 52, 1970.
Webster R and Jackson B.	The Properties of Fired Magnesite Refractories in Oxygen Steel-Making Furnaces. Trans. Brit. Ceram. Soc., 74 (7) 233, 1975.
Kappmeyer K.K. and Hubble D.H.	Pitch-Bearing MgO-CaO Refractories for the BOP Process. High Temperature Oxides Academic Press 1970.
Persson S. and Abdel-Fattah W.	The Influence of Microstructure on the Thermo-Mechanical Properties of Sea Water Magnesite. <u>Ceramica</u> <u>29</u> (4), 1, 1976.

Borisov V.G. and Kravetz L.V. — Refractories (Russia) 34, (9) 562, 1969.

Pawlowski S. and Raz Z. — Phosphate Bonding of Limestone & Dolomite Szklo Ceram. 27 (3) 63, 1976.

Serry M.A. — Resistance of some Dolomite Refractories to Slag Attack. Sprechsaal 111(10) 625, 1978.

Staron J. — The Significance of Firing Temperature of Basic Refractories. 29 (2) 81, 1977.

Girgis L.G. Serry M.A. and Embabi M.K. — Phase Composition and Reactions in Semi-Stable Dolomite Refractories, Sprechsaal 109 (11) 670, 1976.

Leonard L.A. — Dolomite & Silica Refract. J. 53, (5) 12, 1978.

Bendikov A.V. et al — Properties of Tar-Bonded Refractories, Refractories 18 (7), 386, 1977.

Osterreichisch-Amerikanische Magnesit AG — Unfired Basic Composition Br. Patent. 1,419, 795, 1975.

CHAPTER V (potential uses)

Houseman D.H. — Refractories and New Steel-Making Processes. Steel Times 206 (10) 903 1978.

Houseman D.H. — The Basic Oxygen Steel-Making Process - Refractories. Ind. Refr. Makers Assoc. J. 8 (4) 13, 1975.

Spencer D.R.F. May J., and Ball N. — Electric Arc Furnace Refractories. Trans. Brit. Ceram. Soc., 72(3) 125, 1973.

Spencer D.R.F. & Ashworth E.A. — Developments in LD Refractories. Refract. J. 8, 1975.

Dolomite Bricks for Refractory Linings. Cem. Technol. 6 (5) 180, 1975.

Nadachowski F. — Lime Refractories Interceram. 24(1)42, 1975.

Kaufman J.W. & Aguirre C.E. — AOD Practice. Ind. heat. 45(4) 12, 1978.

Steetley (Mfg) Ltd. — Refractory Shapes using Additives. Brit. Patent. 1,441,095 & 1,422,247, 1976.

Steetley Minerals Ltd.	Method for Making Refractory Articles. Br. Patent. 1,486,352 1977.
Bron V.A. and Kharitonova G.S.	Technological Trials with the Dolomite of the Lisegorsk Deposits. Refractories 17(8) 474, 1976.
Ghirotti P.L. et al.	AOD Converter Linings. Refrattari 6(2) 77, 1978.
Muller C.	Present State of Development in the Construction of Torpedo Ladles. Sprechsaal 109(3), 156, 1976.
Hofges H. et al.	Linings for Torpedo Ladles. Tonind. Ztg. 100 (4) 146, 1976.
Van Konijnenburg JT	Wear on Steel Converter Linings. Klei Keram 29 (1) 2 1979.
Baum R.	Dolomite in Stainless Steels. Interceram. 27, 1978.
Spencer D.R.F.	Developments in Basic Refractories. Trans. Brit. Ceram. Soc., 71 123, 1972.
Lakin J.R.	Refractories in Electric Arc Furnaces. Iron & Steel 163, 1971.
Halm L.	Magnesia and Dolomite Refractories. J. Brit. Ceram. Soc., 7, 42, 1970.
Gilpin W.C.	Pitch-Bonded Dolomite Refractories. Refract. J. p. 68, 1969.
Alcock S and Spencer D.R.F.	Basic Refractories in Secondary Steel-Making Ladles. Trans. Brit. Ceram. Soc. 77, 2 1978.
Peatfield M. and Spencer D.R.F.	Refractory Materials for LD Linings. Iron and Steel-Making 5, 221, 1979.
Nagai S. and Hiyama S.	Refractories in Oxygen Steel-Making. Iron & Steel Inst. 60, 1962.
Lakin J.R.	Refractory Materials in Steel-Making. Chem. Eng. CE55 March 1963.
Stradtmann J and Hundt L.	Dolomite in Steel-Making. Fachberichte 15,5,1977.
Industrial Minerals	Refractories, 1 Changing Patterns of Consumption p 15, February 1978.

Kreutzer H.W. et al. — Refractory Linings for EAF in W. Germany. Stahl. U. Eisen 6, 223, 1974.

Howe R.A. et al. — Attack on Periclase Refractory by Dolomite BOF Slag. Am. Ceram. Soc. Bull 55(2)205, 1976.

Kandianis F. and Danilidis P. — Basic Refractories, Production and Application. Interceram. 25 (1) 21, 1976.

Kraner H.M. — Refractories in the U.S.A. Amer. Ceram. Soc. Bull. 56(7) 651, 1977.

Osborn E.F. — Phase Diagrams & Refractories. Amer. Ceram. Soc. Bull. 56(7) 654, 1977.

Sorokin M.A. et al — Refractories for the Converter Lining Refractories 15(5) 317, 1974.

Santamaria F.S. — The Present State of the Cement Technology Refractories Bol. Soc. Esp. Ceram. Vidrio 15(5) 283, 1976.

Hotz G. and Bartha P. — Present Position of Refractory Lining Consumption for Rotary Kilns. Cem. Technol. 7 (5) 170, 1976.

Shubin V.I. — Refractories for the Sintering Zone of Cement Kilns, Refractories. 17 (7) 451, 1976.

Hargreaves J. — Ladle-Lining Refractories. Refrac.J. 53 (6) 11, 1978.

Munchberg W. — Dolomite in Rotary Cement Kilns. Tonind. Ztg. Fachber 102(3), 135, 1978.

CHAPTER VI

Ayers R.F. and Barr H.W. — Refractories Shipments and Energy Costs for Production. Ind. Heat 43 (2), 61, 1976.

Production Figures for Various Refractories in the U.S.A., Czechoslovakia, Yugoslavia and Poland. Sprechsaal 109 (2) 110 1976.

Colle H. — Planning and Construction of up-to-date Production Plant for the Refractories Industry. Ziegel-Industrie 12 454, 1975.

Ghose S.S. et al — Refractories for Basic Oxygen Steel-Making in India. Ind. Refr. Makers Assoc. J., 8(3) 11, 1975.

Gavrish D.I. et al — The Range of Refractories. Refractories 18(11) 621, 1977.

Drum J.C. and Tangney S. — Planning a Sea Water Magnesia Plant. Trans. Brit. Ceram. Soc. 77(4), 10, 1979.

Smirnov G.N. and Sobolev V.V. — Automatically Controlled Plant for Impregnating Converter Refractories with Pitch. Refractories 16 (12) 750 1975.

Spanish Standards Committee — Dolomite Refractories. Span. Stand. UNE 61 028 1975.

Zhukov A.V. et al — Fixed & Variable Costs of Refractories Production. Refractories 19(8) 430, 1978.

Hodson P.T.A. and Padgett G.C. — Current Trends in the use of Refractories. Ind. Heat 46 (2) 48 1979.

Piatowski W. — Kilns & Firing in the Refractories Industry. Ceramurgia 8 (3) 141, 1978.

Jackson B. — Refractories Technology & Output 1950-75 Refract. J. 5, 12, 1977.

Lancujade P. — Use of Refractories in France 1963-69. Refrattari. Lat. I (3) 4, 1976.

Balajiva K. — The Iron & Steel Industry of Thailand. ASRCT Bangkok 1974.

Bhuntumkomol K. et al — Recovery of Chemicals from Thai Bitterns. ASRCT Bangkok 1976.

Zhukov A.V. and Shchelkonogova V.N. — Profit. Indices of Refractories Production. Refractories 17 (3) 148, 1976.

Colle H. — Production Line for Tar-Bonded Refractories. Interceram. 25 (4) 252, 1976.

GENERAL

Rait J.R. — Basic Refractories. Iliffe London 1950.

Chesters J.H. — Steel-Plant Refractories 1972.

Grimshaw R.W. — Chemistry & Physics of Ceramic Materials Benn, London 1971.

White J. — Refractory Materials Vol. 5., Acad. Press, N.Y. London 1970.

Boynton R.S. — Chemistry & Technology of Lime and Limestone Interscience N.Y. 1966.

Riley J.P. and Skirrow G. — Chemical Oceanography. Academic Press 1975.

Mining Annual Review (yearly)

World Mining Annual Review March (yearly)

Budnikov P.P. — The Technology of Ceramics and Refractories (Russian) translation Arnold (London) 1964.

Alper A.M. — High Temperature Oxides Part I Magnesia, Lime and Chrome. Acad. Press N.Y. 1970.

Alper A.M. — Phase Diagrams. Acad. Press N.Y. 1970.

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