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THE PREPARATION OF SMALL DENSE CRUCIBLES OF MAGNESIA

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THE PREPARATION OF SMALL DENSE CRUCIBLES OF MAGNESIA*

ABSTRACT

Methods are described for making small magnesia crucibles possessing smooth, non-porous surfaces. Carbowax 4000 was the best temporary bond and lubricant of the many tested. Typical dies for pressing crucibles are shown and a small oxy-propane furnace is described for firing crucibles up to 1900°C.

1. Introduction

When reductions and remeltings of uranium and similar metals are carried out on a small scale best results are obtained in refractory crucibles which possess smooth, non-porous surfaces. Such surfaces minimize penetration and attack by the slag and metal thereby giving higher yields and a purer product. It is likewise necessary that the refractory material be stable to the reactants and products of the reaction. Furthermore, it is often necessary that these crucibles meet rigid size specifications. In general, these requirements eliminate the use of permanent plasticizers and binders (e.g., clay) for the non-plastic oxides such as MgO, BeO, and ThO_2. In place of clay, temporary organic binders are used to help form the crucibles.

Because it was necessary to utilize the equipment available, the details of the procedure which follow should not be considered as ideal for production of large quantities, but as a guide to the laboratory preparation of this type of ware.

2. Raw Materials

2.1 Fused Magnesia. The initial work on this development was done with fused magnesia containing about four per cent silica. This amount of silica, however, proved excessive as shown by the high silicon content of the uranium prepared in such crucibles. It was necessary to reduce the

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*Based on CT-2780, CT-2699, CT-2619, CT-2472, CT-2387, and CT-2252.

amount of silica to about two per cent by adding pure calcined magnesia. Fused magnesia was purchased from the General Electric Company in 190 pound drums. The particular batch used in this work had the grain-size distribution and chemical composition shown in Tables 1 and 2 respectively.

TABLE 1

SCREEN ANALYSIS OF FUSED MAGNESIA
(General Electric Company)

Mesh Tyler Series	Per Cent Finer
48	92.6
65	65.3
100	36.9
150	21.6
200	10.9
325	5.9

TABLE 2

CHEMICAL COMPOSITION OF FUSED MAGNESIA

Constituent	Amount, Per Cent
SiO_2	4.82
Al_2O_3	0.05
Fe_2O_3	0.035
CaO	1.50
Alkalis	0.03
MgO, by difference	93.57

The silica and lime were present in this product as monticellite ($MgO. CaO. SiO_2$) or a solid solution of forsterite ($2 MgO. SiO_2$) and monticellite. The optical properties of these two compounds are so nearly alike that it was very difficult to make an accurate petrographic analysis. There was no evidence of solid solution of Fe_2O_3 or other oxides in the periclase grains, or of inclusion of CaO crystals.

2.2 Calcined Magnesia. Reduction of the silica content of the crucibles was accomplished by mixing fused magnesia with calcined pure magnesia (U.S.P.-XII, Heavy Calcined, purchased from Mallinckrodt Chemical Works). Since the U.S.P. material as received was too fine it was made somewhat coarser by calcining in a gas-fired kiln to 1300°C. In this operation, the magnesia was loaded into large magnesia crucibles about three inches in diameter and 10 inches high and calcined according to the schedule shown in Figure 1.

After calcination the product was crushed by hand and stored in bottles. The chemical composition of the Mallinckrodt magnesia as received was as follows:

TABLE 3

CHEMICAL COMPOSITION OF MALLINCKRODT, U.S.P.-XII, HEAVY CALCINED MAGNESIA

Constituent	Amount, Per Cent
SiO_2	0.30
Al_2O_3	0.11
Fe_2O_3	0.031
CaO	1.06
MgO, by difference	98.50

During calcination the average size of the individual crystals increased from about 2 to 8 microns. Silica and lime were present as birefringent silicates similar to that in the fused material.

3. Processing of Raw Materials

3.1 Mixing and Grinding. The batch composition selected consisted of equal weights of fused and calcined magnesia, mixed with 12 per cent by weight of Carbowax 4000, the latter serving as a lubricant and temporary binder. This composition was selected because tests showed it to be quite satisfactory for production use.

The magnesia was ground 15 hours in one-gallon porcelain lined mills, loaded with one-inch diameter Porox balls, operated at 54 rpm. (Porox balls may be obtained from The Patterson Foundry & Machine Company, East Liverpool, Ohio.) The weight of balls used was 4.5 times the weight

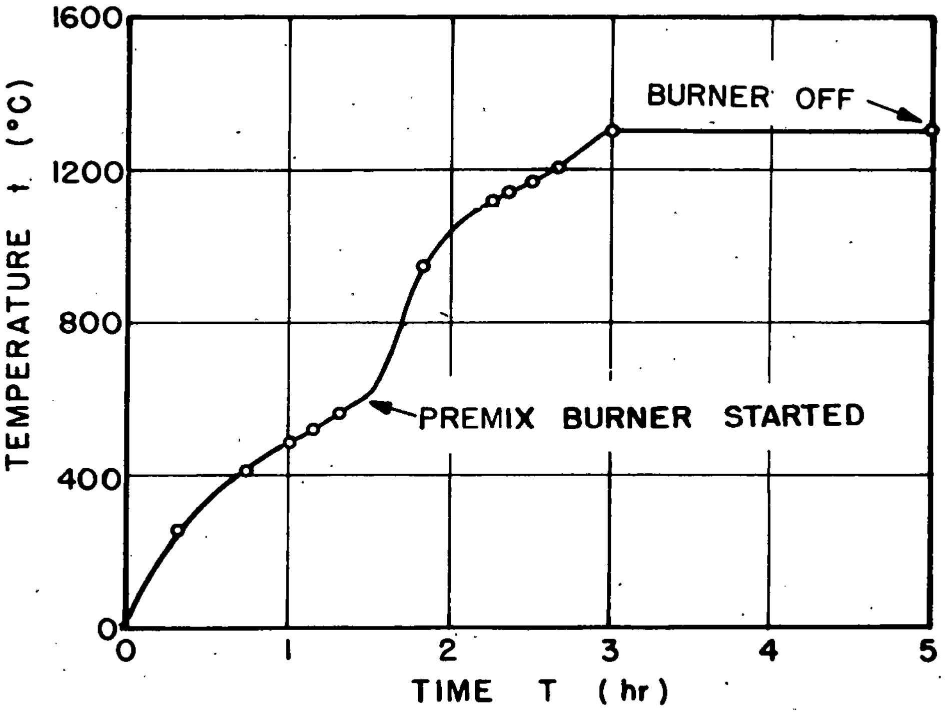

Figure 1. Heating curve followed during calcination of U.S.P. magnesia at 1300°C. Air-gas burners used to 600°C and a Premix burner for heigher temperatures.

of magnesia. Because of reaction between magnesia and water, 95 per cent ethyl alcohol was used as the grinding medium. A typical mill loading is given in Table 4.

TABLE 4

TYPICAL CHARGE FOR BALL MILLING MAGNESIA

Material	Amount, grams
Fused MgO	500
Calcined MgO	500
Porox balls	4500
Alcohol	670

During grinding there was a silica "pick-up" from the mill of about one per cent which resulted in a total silica content of about 3.6 per cent.

3.2 <u>Drying the Mix</u>. After grinding, the mixture was poured into large evaporating dishes and dried in a gas oven with forced draft at 105° to 110°C. The mass was stirred during drying to minimize segregation and to prevent the formation of a hard crust; lumps were broken up as rapidly as they formed. It was essential to continue drying until the last trace of alcohol had been removed. Residual alcohol apparently had a deleterious effect on the Carbowax, which resulted in a greater number of cracked crucibles. At least 24 hours was required for the drying process.

After drying it was necessary to break down further any lumps present by shaking the material through a 65 mesh screen on which were placed four small porcelain balls. Table 5 shows the grain-size distribution of the magnesia at this stage as obtained by the hydrometer method(1) using absolute methyl alcohol for the settling medium.

Dispersion of the sample was accomplished by a 15 minute ball milling with a large excess of liquid and five porcelain balls in a one-quart mill, followed by tumbling overnight in a bottle with additional liquid (equivalent to a five per cent suspension).

TABLE 5

GRAIN-SIZE DISTRIBUTION OF MAGNESIA AFTER MILLING

Diameter of Equivalent Sphere in Microns	Per Cent Finer
74	100.0
44	99.8
28.0	95.0
20.2	92.2
14.3	90.5
11.9	88.3
9.3	83.8
6.95	74.5
5.0	62.9
4.3	54.6
3.3	37.0
2.41	23.7
1.98	14.4
1.30	3.9
1.01	1.1

3.3 Incorporating the Lubricant. It is desirable to use a lubricant and temporary bond in molding non-plastic materials to insure adequate flow to all parts of the mold, to reduce forming pressures required, and to give strength to the unfired piece. When a proper lubricant has been selected the pressed ware will release from the mold cleanly, have a smooth surface, and fire to a uniformly high density. Usually the lubricating and bonding qualities can be found in a single organic product; sometimes, however, it is necessary to employ a mixture. Many materials may be used for this purpose, but of those tested Carbowax 4000 (a polyethylene glycol obtained from the Carbide and Carbon Chemicals Corporation) proved to be the best under the limitations imposed by the equipment available.

Incorporation of Carbowax 4000 probably could have been done best with a small muller, but because the batches were small, mixing was carried out by hand in a large flat porcelain mortar. An aqueous solution of Carbowax 4000 was made up so that 2 cubic centimeters of solution contained one gram of Carbowax. A volume of solution was worked into the magnesia until it contained 12 per cent by weight of Carbowax 4000. To facilitate granulating, the wet mixture was then dried slightly at a temperature below 80°C to prevent decomposition of the Carbowax 4000. Prolonged contact of the mixture with water was avoided.

3.4 Granulation. By granulating the powdered material before pressing there resulted a considerable compacting and hence, reduction of bulk density of the magnesia, as well as improved flow into the mold. The batch was granulated by passing the damp material through a 14-mesh screen. Excessive fines indicated that the material was too dry; excessive coarse granules, too wet. All the magnesia was made to pass through the screen by rubbing and shaking.

3.5 Drying after Granulation. After granulation, the material was placed on shallow trays and dried at 60° to 80°C. Using a convection drier at 75° to 80°C, 1.5 hours was necessary; with an ordinary electric oven a minimum of 2.5 hours was required. It was undesirable, however, for any water to remain because it resulted in sticking of the magnesia to the mold parts. Most satisfactory results were obtained by shorter drying periods at 75° to 80°C as opposed to longer times at 50° to 60°C. After drying, the granulated material was allowed to cool in the open and was then stored in bottles.

3.6 Lubricants other than Carbowax 4000. In addition to Carbowax 4000, investigations were carried out on paraffin-stearic acid emulsions, Carbowax 1500, Carbowax 6000, lard, phenol-formaldehyde resins, and polyvinyl alcohol solutions. Carbowax 4000, however, proved to be best. Paraffin-stearic acid emulsions gave good mold release and fair internal lubrication, but the pressed crucibles were not as dense as those formed with Carbowax 4000. Phenol-formaldehyde resins were too difficult to use because of the higher pressing temperatures that had to be maintained within close limits for relatively long periods while the resin cured. The indications were, however, that these resins would have been superior to any of the other lubricants. The others mentioned gave relatively poor results.

4. Method of Pressing Crucibles

4.1 Dies. The dies used for pressing crucibles were made of "Crocar" steel hardened to 58 to 62 Rockwell "C". Four sizes of crucibles were made, the largest being 1.5 inches high and 1.0 inch in diameter. Difficulties in manufacture increased with the size of the crucible. The shape of the crucible interior also affected the difficulty of production: a spherical inside bottom was the easiest shape to produce; a flat bottom, the most difficult. Figure 2 shows a typical die. All surfaces in contact with ceramic material were fine ground and polished; clearances between moving parts were about 0.001 inch. The taper in the mold box was large enough to permit release of the pressed crucible with very small upward movement. (Cracks attributable to inadequately tapered dies usually could not be detected until after preoxidation or final firing.) An added advantage of generous taper was that it compensated for the tendency the crucibles had to "pull in" at the top during firing.

During the pressing operation, it was necessary that only the plunger be allowed to move. When the bottom plug was made long enough to extrude the crucible from the die, the mold box was supported on a hollow cylinder. The length of this cylinder was such that the plug came to the exact position in the mold box where the bottom of the finished crucible was located. This was at the point where the taper began, usually one inch from the bottom of the mold box. The cylinder on which the mold box was placed was mounted permanently on a flat plate, enabling the operator to lift the assembly without disturbing the position of the bottom plug. (The need for this supporting cylinder could be eliminated by making the bottom plug only one inch long. In that case, however, a supplementary longer rod would be necessary to eject the crucible.)

4.2 Heating of Dies. When Carbowax 4000 was used as the lubricant the dies were heated to 30° to 40°C, either by playing a flame on them, by using an electric heater jacket mounted around the mold box, or by placing them on a hot plate. Temperature "control" was maintained by touch. When the die was too hot the surface of the crucible became pasty, and there was excessive flashing around the top and bottom rams of the mold. Also, hot dies caused a greater amount of cracking when the Carbowax 4000 was

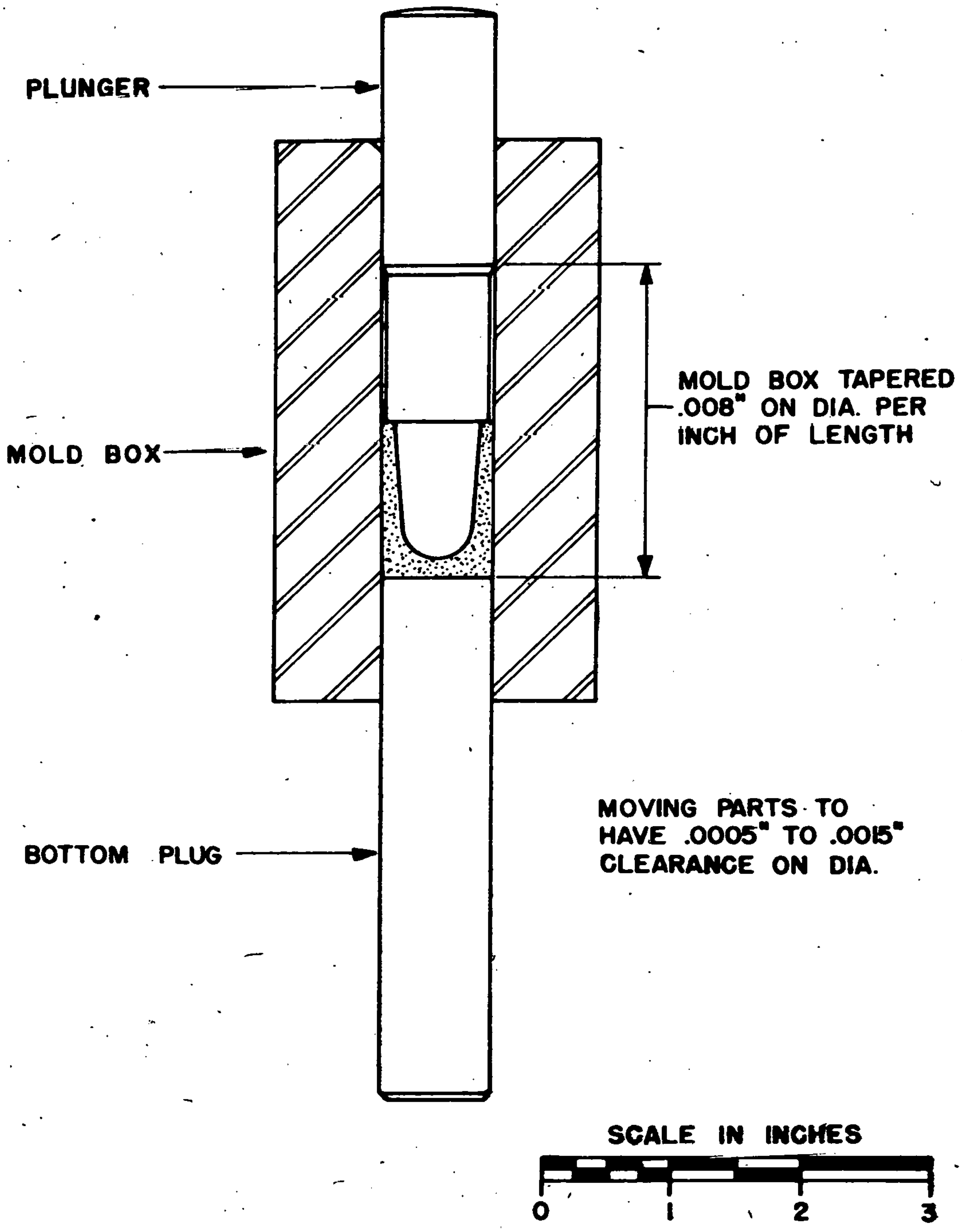

Figure 2. Die assembly for pressing small crucibles (A-203).

burned out. When the die was too cold the granules failed to break down adequately and there was lack of flow of material to the top of the crucible wall. Figure 3 shows the manner of mounting the electric heaters. (The heaters may be obtained from The Hevi-Duty Electric Company, Milwaukee, Wisconsin.)

4.3 The Press Used in Pressing. A Watson-Stillman hand-operated press (Figure 4) was used with 12 x 12 inch platens, 4.5 inch stroke, and with 30 tons capacity on a 3.5 inch ram. (The posts were lengthened so that as much as 18 inches of daylight could be obtained.) The very short stroke of the press made it inadvisable to mount the die parts permanently in the press, a condition almost indispensable for hot pressing or commercial production.

4.4 Pressing. The procedure developed for the types of crucibles produced varied considerably. The first crucibles, Type N (Figure 9), were formed at pressures as high as 70,000 psi. As the pressing mixture and die designs were improved, lower pressures were found desirable. Moreover, with lower pressures less cracking was found to occur during the oxidation of the Carbowax 4000.

Type D-4a (Figure 9) crucibles were formed at about 50,000 psi with the die heated "hot to touch". This type of crucible was quite easy to produce. Type A-203 (Figure 9) with spherical bottom was produced by pressing in a "lukewarm" die to 30,000 psi. Type A-204 (Figure 9) was produced by the "preforming" method described below.

A method of reducing the differential shrinkage in diameters, called "preforming", consisted of pressing a crucible at 40,000 psi, breaking off the bottom, placing the remaining side wall in the die, adding sufficient additional material to form the bottom, and then pressing to 20,000 psi. Satisfactory crucibles were made by this method but it was found to be too time-and material-consuming for producing large numbers of crucibles.

5. Removal of Organic Lubricant

Organic binders and lubricants were removed with great care to reduce cracking and blistering of the crucibles; sometimes these defects were observed in the preoxidized crucible, at other times not until after

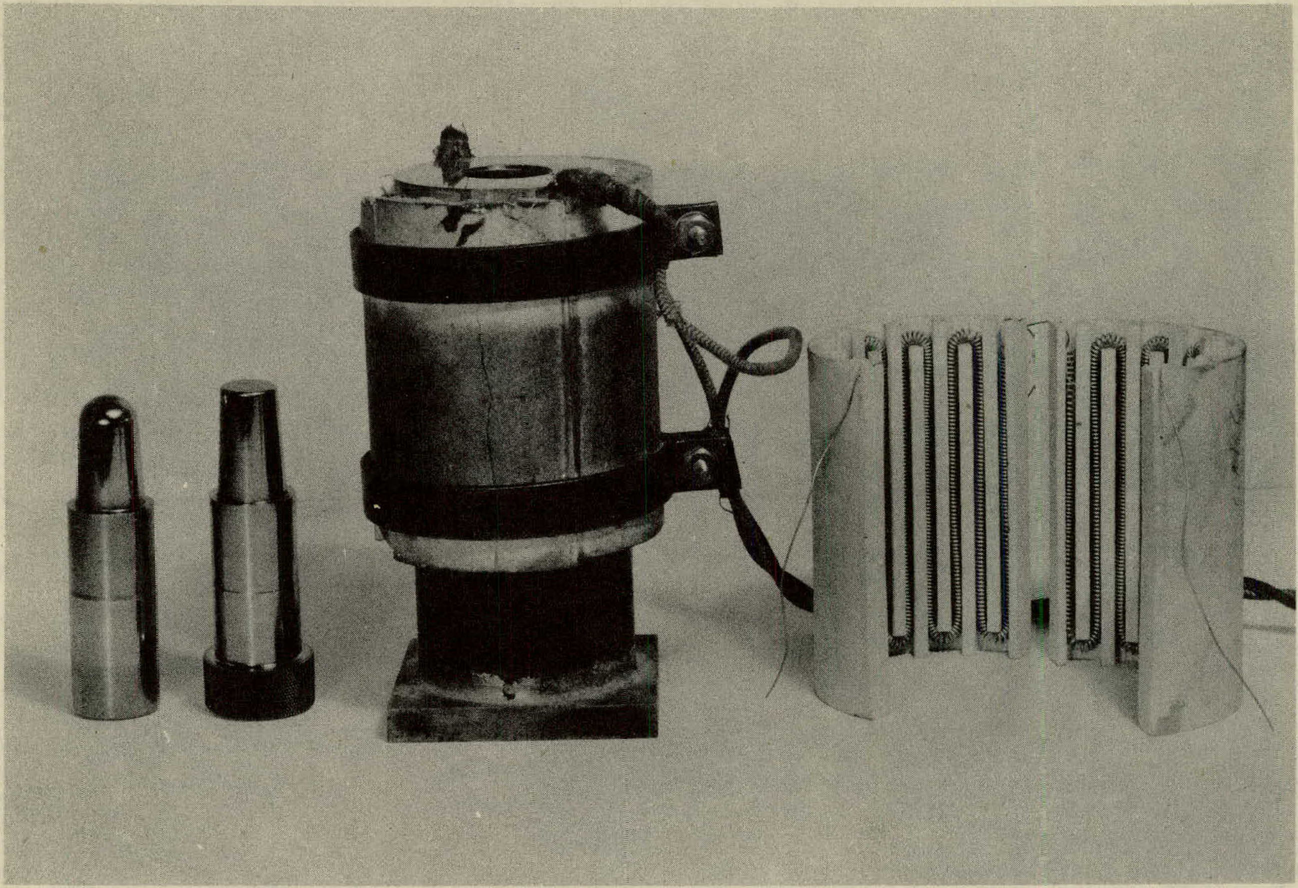

Figure 3. Photograph of die for pressing Type A-204 crucibles. At the left are two shapes of plungers for forming the inside of the crucibles; in the center is a mold box resting on a cylinder of correct height to keep pressing ram at proper level during pressing; at the right is an unmounted heater.

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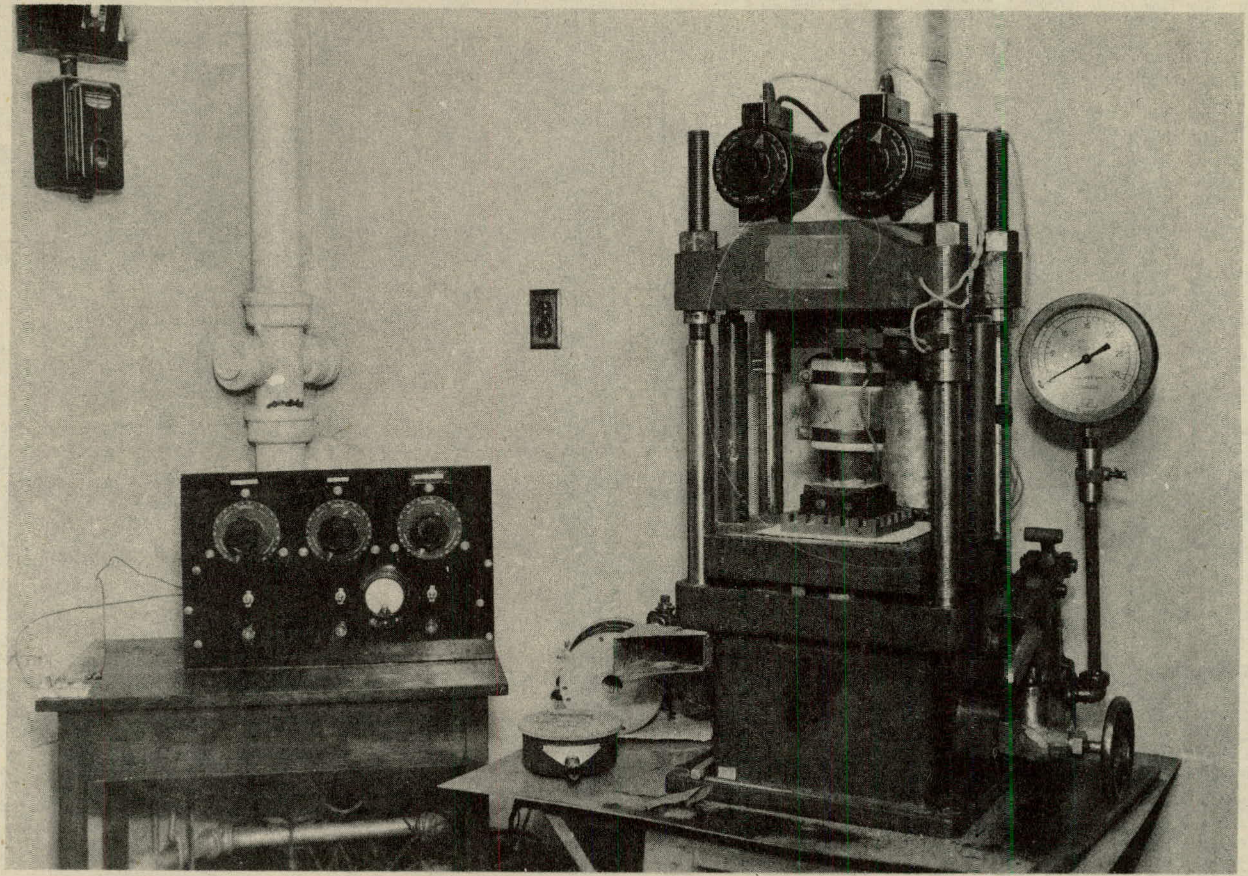

Figure 4. Photograph of press used in molding small crucibles with an A-204 die in place. The cartridge heaters may be seen mounted in the steel plate under the die; the grid below is to prevent overheating of the bottom platen. The Variacs are for control of the various heating elements.

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firing. Proper conditions for removal of Carbowax 4000 or resin were obtained by placing the crucibles in covered saggers and heating to 500° to 600°C in an electric furnace at a controlled rate (see Figure 5). Saggers were made by coring the centers of soft insulating fire bricks and grooving the tops of the sides to permit escape of gases and entrance of air (Figure 6). Later work showed that when lower forming pressures were used the heating schedule could be shortened to 15 hours.

The same heating schedule (Figure 5) was used to oxidize crucibles bonded with paraffin emulsion. It was necessary, however, to place such crucibles not in closed saggers, but directly inside the oven on wire gauze to insure evaporation of the paraffin at the bottoms of the crucibles.

The furnace door was always closed tightly, and it never affected results to place crucibles containing all three types of bonds in the furnace at the same time. Often both Carbowax 4000 and resin-bonded crucibles were placed in the same saggers.

6. Firing of Crucibles

Magnesia crucibles were fired to 1740° to 1760°C and held at this temperature for about 45 minutes to one hour. Figure 7 shows the small up-draft kiln in which the crucibles were fired; it consisted of a 9 inch by 9 inch by 6 1/2 inch chamber lined with pure alumina brick and insulated with insulating fire brick. Pure alumina brick may be obtained from the Norton Company under their trade name Alundum Brick No. 1190. Crucibles were placed on individual setters of the same composition as the crucibles with coarse-grained grog of fused low-silica magnesia sprinkled on the setters to prevent them from sticking to the crucibles. Later, individual shrinkage plates were found to be unnecessary and the crucibles were set on large magnesia setters, using grog, and the setters placed directly on the alumina brick floor. Initial heating was done with gas-compressed air burners, and the temperature measured with a thermocouple of platinum and platinum alloyed with 10 per cent rhodium. For temperatures above 1100°C a Leeds & Northrup optical pyrometer was used. At about

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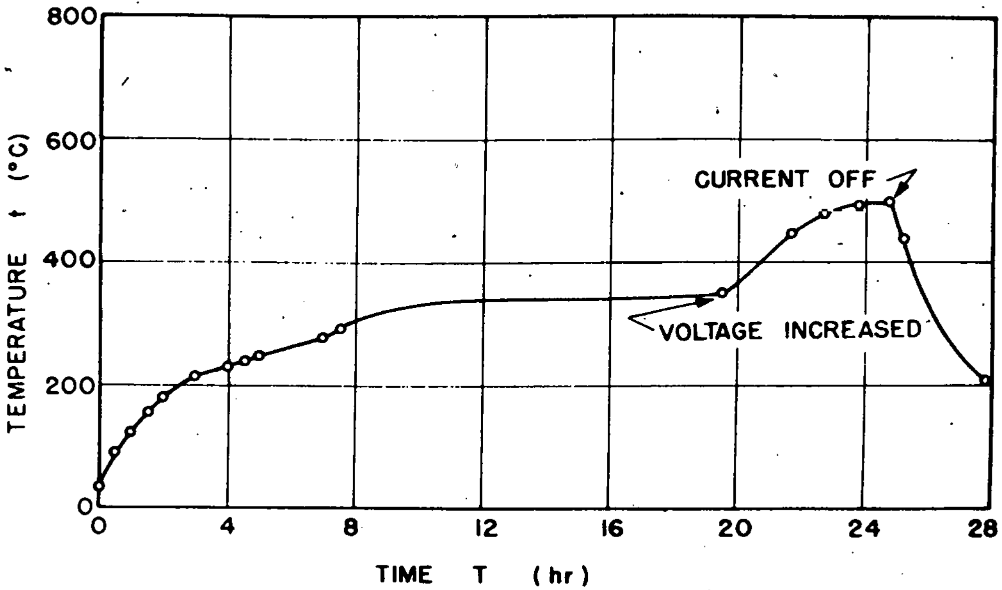

Figure 5. Heating curve followed during oxidation of organic bonds in pressed crucibles.

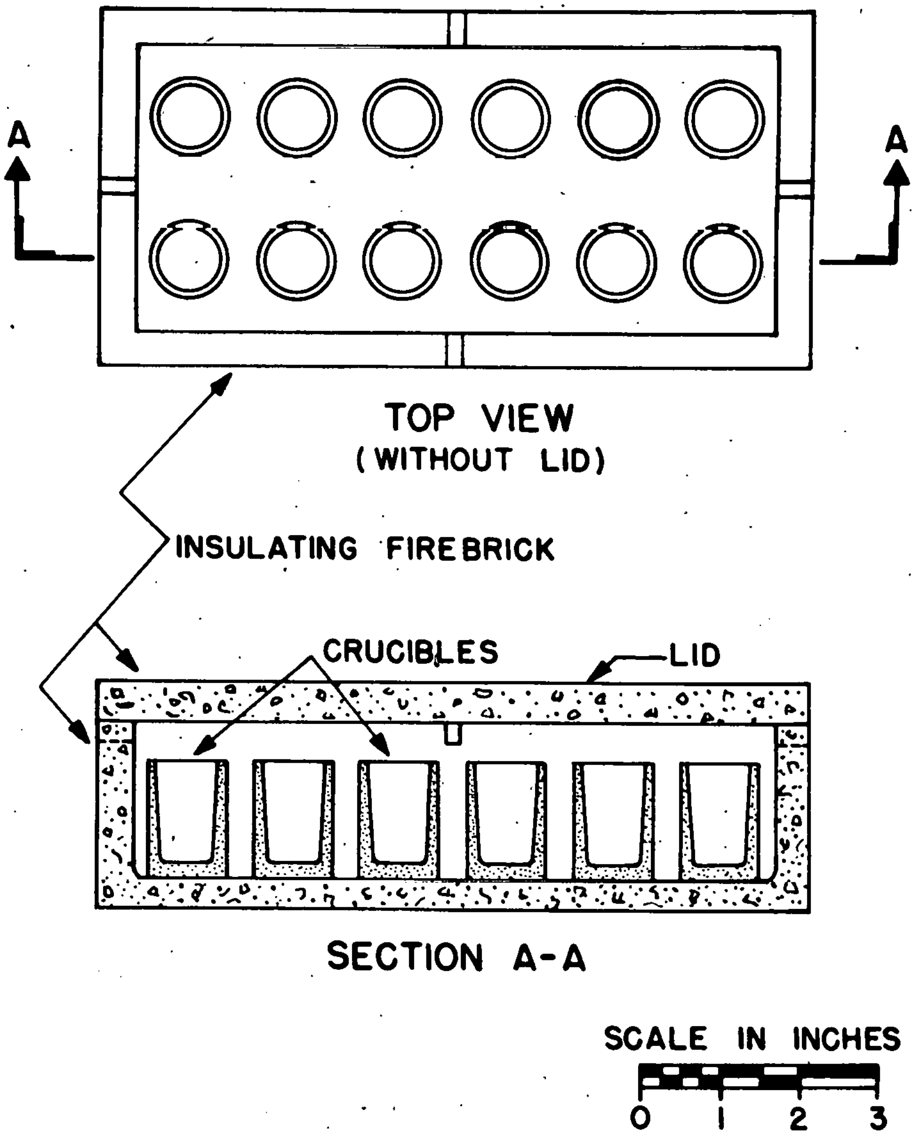

Figure 6. Sagger, made from insulating brick, showing crucibles in place for burning out binder and lubricant.

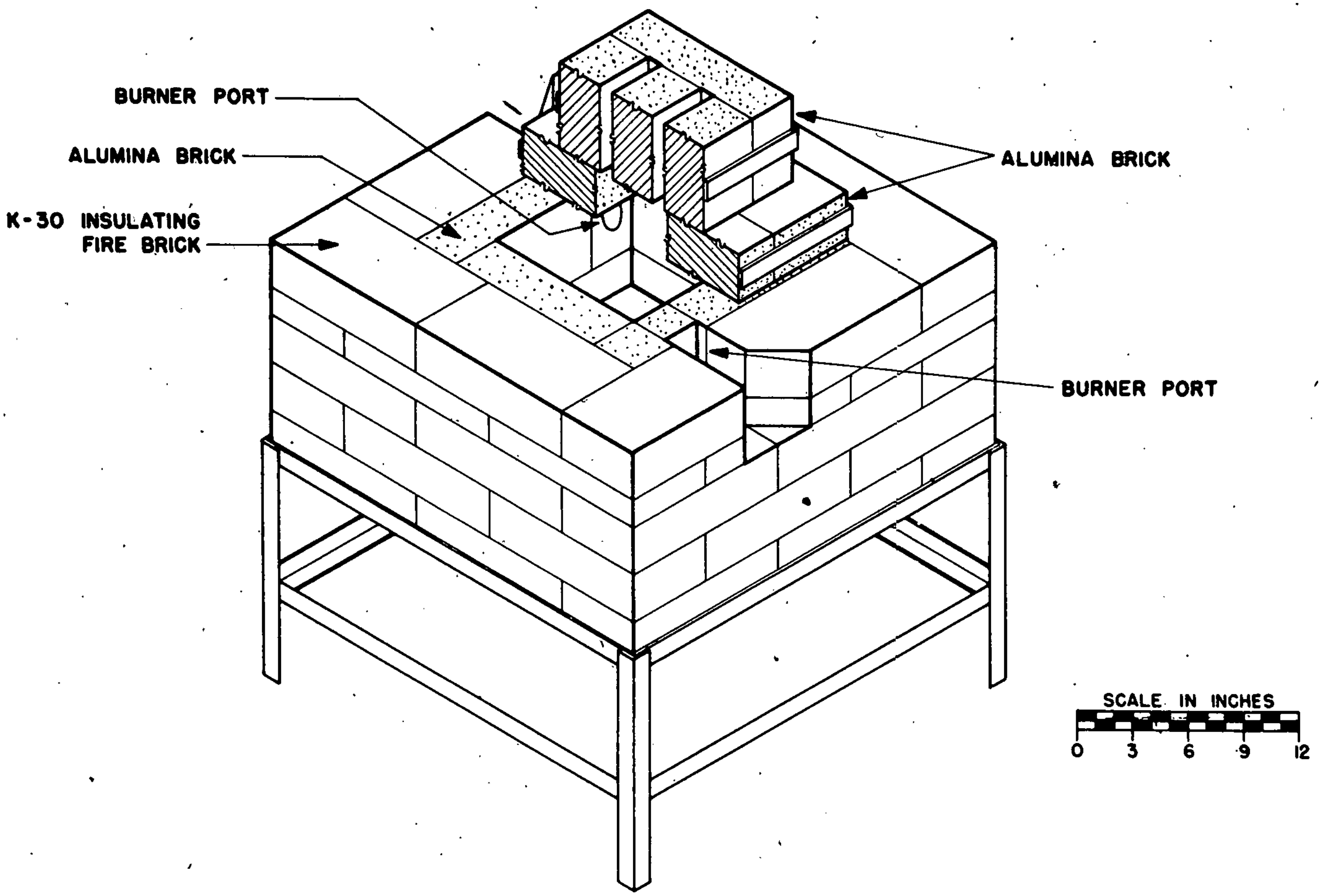

Figure 7. High-temperature furnace for firing crucibles up to 1900°C with oxy-propane burners. Lid is held together by steel bands and can be lifted as a unit. (No cement was used in laying the pure alumina bricks.)

1100° to 1200°C oxy-propane burners were substituted and the firing completed with them. A typical heating schedule is shown in Figure 8. For a single fire on the schedule shown there was required about 90 cubic feet of propane and 360 cubic feet of oxygen. Oxygen cylinders were connected through a manifold system in order to maintain a steady supply of oxygen throughout a fire.

7. Defects and Their Control

7.1 Cracking. The most serious defect encountered in the production of small dense magnesia crucibles was cracking. It usually occurred either in oxidation of the Carbowax 4000, in the final firing of the crucibles, or in other steps of the general process. The most common cracks were small ones radiating from the center of the bottom, and also cracks on the crucible side parallel to and near the bottom.

Prolonged contact of magnesia with water was avoided because many experiments indicated that the presence of water caused cracking.

The characteristics of Carbowax 4000 as well as of the magnesia probably caused these discrepancies. Variations in various lots of Carbowax 4000 also caused cracking. Experiments showed that a purer form of this material, Carbowax 4000W, caused more cracking than the regular material.

The pressure of forming was considered the most serious source of cracking with higher pressures giving increased cracking. Pressures were reduced as low as possible to produce non-porous crucibles with low differential shrinkage between top and bottom diameters.

Adequate tapering of the dies was found essential in minimizing cracking. Dies with no taper required high extrusion pressures and resulted in dragging the crucible against the die walls, thus leaving stresses in the crucibles.

Too high temperatures of the die during pressing also caused cracking: as the crucible size increased, the pressing temperature had to be decreased to nearly room temperature.

The heating rate and atmosphere during oxidation of the Carbowax 4000 were very important--expecially so before the volatile part of the wax had

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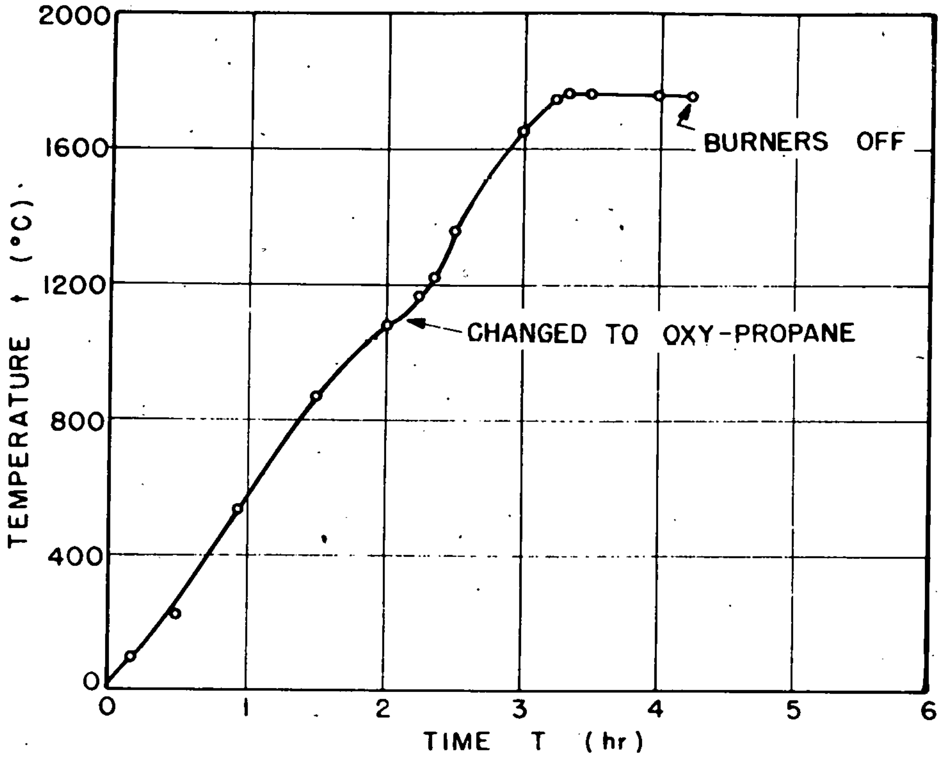

Figure 8. Heating curve followed during firing of magnesia crucibles to 1750°C.

been driven off (around 200°C). Lower forming pressures allowed the oxidation schedule to be shortened.

When firing of crucibles was begun, little concern was given to the heating schedule and cracking occurred irregularly. A series of firings with variations of the heating rate was conducted, indicating that the schedule shown in Figure 8 was the shortest possible one in which crucibles could be safely fired. After this schedule was developed, little cracking occurred in firing. Occasionally, crucibles which were apparently uncracked before firing cracked during firing. This was thought, however, to be caused by the inherent stresses remaining in the crucibles after pressing.

When crucibles were made on a production scale, defects usually disappeared until the last few lots yielded as high as 90 per cent satisfactory crucibles.

7.2 Blistering. As described in the following section, when the temperature of firing was carried above 1740° to 1760°C, blistering occurred. Certain areas of the kiln floor were found to be considerably hotter than the average temperature and blistering usually occurred when crucibles were placed in these areas. Another type of blistering was produced by localized impurities picked up during the processing, as when particles of grinding ball chipped off during the milling operation, or when foreign particles were blown against the crucible surfaces during firing, as often happened if the oxy-propane burners were not properly adjusted at all times.

8. Properties of Fired Magnesia Crucibles

The fired magnesia crucibles, shown in Figure 9, were white, translucent, and possessed a smooth matt surface. There was no dye absorption, indicating that nearly all pores were closed—at least all of those connected to the surface of the crucible. The density varied from 3.20 to 3.35 showing that in some cases there were more closed pores than in others. Shrinkage varied from 9.7 to 11.3 per cent with the average being about 10.5 per cent. Petrographic examination of finished crucibles

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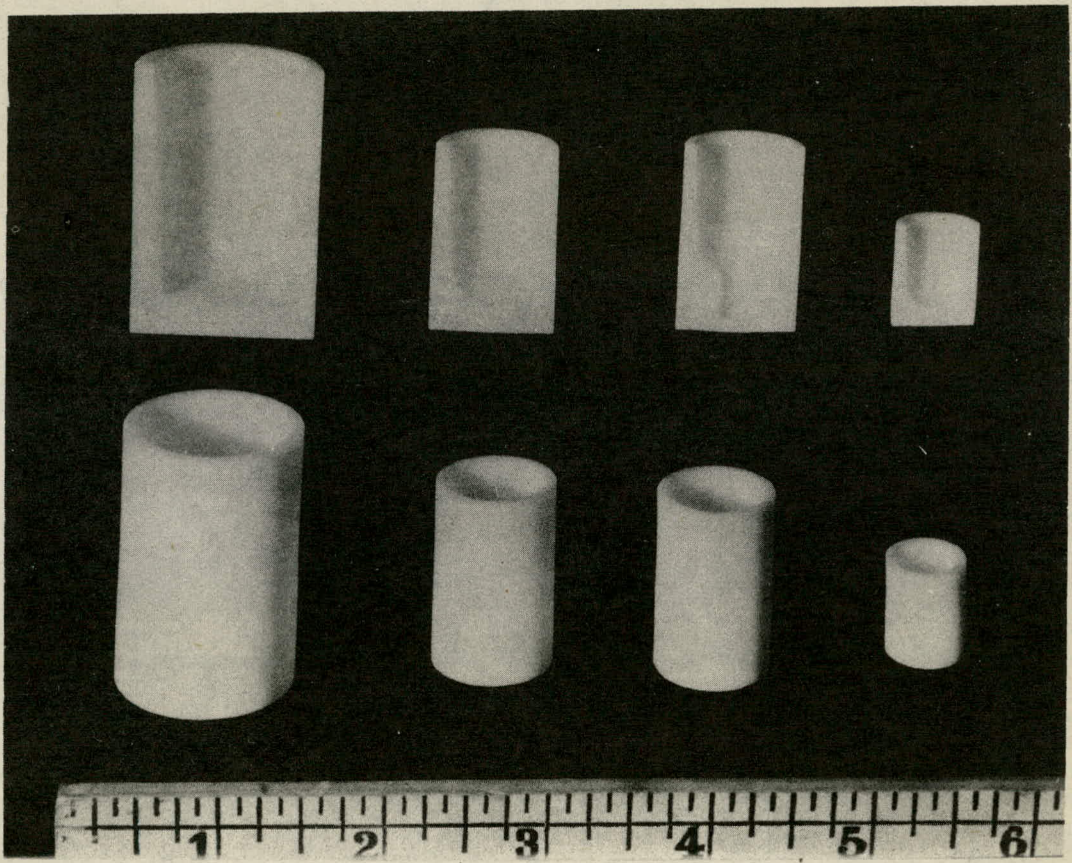

Figure 9. Typical magnesia crucibles: from left to right, types A-204, A-203, D-4a, and N. Scale at bottom is in inches.

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showed that the grains of periclase, rounded and of uniform size, were bonded together with a birefringent silicate material.

That this particular magnesia body had a rather short firing range was indicated by the blisters which developed when the temperature exceeded 1760°C, and by the porosity observed when the firing time at 1760°C was decreased from 45 to 20 minutes.

Chemical analysis of a typical fired crucible is given in Table 7.

TABLE 7

CHEMICAL ANALYSIS OF A TYPICAL FIRED MAGNESIA CRUCIBLE

Constituent	Amount, per cent
SiO_2	3.61
Al_2O_3	0.36
Fe_2O_3	0.03
CaO	1.17
Alkalis	0.06
MgO, by difference	94.77

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