The Complete Technology Book on Asbestos, Cement, Ceramics and Limestone
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Asbestos is the generic term for a group of naturally occurring fibrous minerals with high tensile strength, flexibility, and resistance to thermal, chemical and electrical conditions. Asbestos fibers are of high-tensile strength, flexible, heat and chemical resistance, and good frictional properties. Cement is the most essential raw material in any kind of construction activity. Ceramics also known as fire clay is an inorganic, non-metallic solid article, which is produced by the art or technique of heat and subsequent cooling. Limestone is a sedimentary rock, mainly composed of calcium carbonate (CaCO3). It is the principal source of crushed stone for construction, transportation, agriculture, and industrial uses.

Emerging applications in commercial sectors such as asbestos, cement and ceramic are poised to fuel demand in the coming years. Growing demand for limestone in the production of cement as well as in several other chemicals that are used in the production of high-value everyday products offers significant opportunities for growth. Global Limestone consumption is projected to reach 5.7 billion tons and expected to grow at an average annual rate of 4–5% in coming years. Presently, cement production is 330 million tonnes and expected to double to reach almost 550 million tonnes in future.

The major contents of the book are asbestos, monitoring and identification of air-borne asbestos, asbestos in industrial applications, asbestos – cement products, non – occupational asbestos emissions and exposures, cements, mortars and concrete, raw materials, additives and fuels for cement, processes of manufacturing of cement, cement based on natural and artificial pozzolanas, fast-setting cements, special portland cements, packing of cement, storages of cement, ceramics, lime & limestone, glass & glass ceramics etc. It describes the manufacturing processes and photographs of plant & machinery with supplier’s contact details.

It will be a standard reference book for professionals, entrepreneurs, those studying and researching in this important area and others interested in the field of these industries.

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Sample Chapter:
Asbestos

Asbestos is a broad term applied to a number of fibrous mineral silicates found in the natural state throughout the world. The most extensive deposits are found in Canada in the province of Quebec. Some thirty varieties of asbestos exist, but only six of these are of economic importance. For the purpose of this article, only three of the six will be considered: chrysotile, or white asbestos; crocidolite, or blue asbestos; and amosite. Chrysotile is a fibrous variety of serpentine, a hydrous magnesium silicate mineral. Crocidolite and amosite are member of a group known as amphibole fibers. Crocidolite and amosite are iron silicates of solid-strip structure. The former is a sodium ferroso-ferric silicate found mainly in South Africa and, to the lesser extent, in Australia and Bolivia. The latter is a ferrous magnesium silicate found only in South Africa.

Commercial Uses

Asbestos fibers, because of their great strength, are used as a reinforcement with other raw materials. They are combined with Portland cement to form a variety of structural building materials that are outstanding for their strength and durability. Corrosion resistant asbestos-cement pipe is also produced and can contain a blend of asbestos fibers in combination with Portland cement. Asbestos fiber can also be combined with plastics to form floor tiles which are noted for their wear. Asbestos is also used as reinforcement in lime silica and magnesia products for high-temperature insulations. The flexibility of asbestos fibers enables them to be woven into yarns, cloths, and ropes. Such asbestos fabrics are fire proof, rotproof, and capable of withstanding high temperatures. Asbestos fiber also can be combined with metal, rubber, resins, and other impregnants and binders to form brake linings, packings, and gaskets.

Properties and Composition

The physical and chemical properties of three varieties of asbestos are summarized in Table 1(3). The chemical compositions are shown in Table 2. It should be pointed out that compositions vary and that different sources report different empirical formulae.

Electron microscope pictures of the three type of asbestos fibres chrysotile appears to be a tabular structure with amorphous material on the outside and inside of the tubes. Crociodolite appears to be in straight needles. Amosite molecules seem to form straight flat sheets.

Gravimetric Method. The gravimetric method for silica involves fusion with sodium carbonate solution in hydrochloric acid, dehydration of the silica, and volatilization with hydrofluoric acid.

Procedure

Weight 1.0000 g of ignited sample into a clean, tared platinum crucible. Add approximately 5 g of anhydrous sodium carbonate and mix well. Cover the crucible and heat until fusion is complete. The heat should be gradually increased at first until action ceases and then the full heat of the burner can be employed. Usually 30-60 min is required for complete fusion. Using platinum-tipped tongs, remove to cover and carefully swirl the contents to spread the melt around the inside of the crucible. Allow to cool and then place the crucible and the cover into a clean, 600-ml Pyrex beaker containing approximately 150 ml of 1:6 hydrochloric acid. Cover the beaker and carefully heat on a hot plate until the melt is completely digested. Remove the crucible and the cover the scrub to remove any adhering insolubles. Crush all siliceous lumps thoroughly. No gritty or unfused matter should remain at this point. Should unfused matter be present, the fusion must be repeated. Evaporate to dryness on a steam bath. This evaporation requires several hours. Place the beaker containing dry residue on the hot plate to insure complete removal of all hydrochloric acid. Cool, add 10 ml of concentrated hydrochloric acid to the residue and then add 100 ml of hot water. Heat on the hot plate until all salts dissolve. Filter the precipitated silica using No. 41 Whatman filter paper or equivalent and wash with hot 5% by vol hydrochloric acid. Finally wash with hot water. Scrub the beaker to remove any adhering silica. Transfer the clear filtrate to the original beaker and repeat the dehydration
directly on the hot plate. Exercise care to avoid splattering as the volume decreases. Bake the residue carefully to remove all acid and continue baking on an asbestos pad for 1 hr to dehydrate completely the last traces of silica. Cool, dissolve salt as previously indicated, and filter on No. 40 Whatman paper or equivalent. Wash as previously indicated, and scrub the beaker to recover all silica. Save the filtrate for separation of ammonium hydroxide group. Place both filter papers containing the silica in the tared crucible used in fusion and heat in a muffle furnace at 800°F to char the filter paper. Raise the temperature to 1000°F and heat until all the carbon is removed and the silica residue is white. Then heat to constant weight at 1800°F. Obtain the total weight of the crucible and contents. The residue represents impure silica.

**Manganese.** Since manganese is present in the <0.01% quantity, it is not normally removed prior to determination of calcium and magnesium. However, if the need arises, manganese can be precipitated from the filtrate remaining after removal of the R2O3 group. This separation is required in the analysis of amosite fiber and will be discussed under the amphiboles. In the analysis of chrysotile asbestos, manganese can be determined colorimetrically by periodate oxidation.

**Acid-Soluble Sulfate.** The % acid-soluble sulfate is obtained by digesting the original sample with 10% hydrochloric acid and precipitating the sulfate with barium chloride solution.

**Procedure**

Transfer 3-5 g of the original sample to a 400-ml beaker. Add 100 ml of 10% hydrochloric acid and boil the mixture for 1 hr. Filter using vacuum, and wash the residue with hot water.

Transfer the filtrate to a 400-ml beaker and reduce the acidity to 1-3% by using concentrated ammonium hydroxide. Heat to boiling and slowly add 25 ml of 10% barium chloride solution. Heat on a hot plate until the precipitate settles. Cool and filter on Whatman No. 40 filter paper. Wash the precipitate free of chlorides with cold water. Transfer the precipitate to a tared platinum crucible and ignite at 800°F, 1000°F, and finally at 1800°F to constant weight. Calculate the acid-soluble sulfates from the weight of the barium sulfate precipitate.

**Chloride.** Acid-soluble chloride may be determined by the Volhard method described below. Should watersoluble chloride be desired, an aqueous extraction of a 10% slurry of the fiber in a water-immiscible solvent can be made. Chloride can be determined in the filtrate by any one of several methods suited to this low concentrations.

**Carbon Dioxide.** Carbon dioxide from carbonates is usually very low in quantity in chrysotile asbestos. However, as previously indicated, fibers such as Arizona, California (Coalinga), and Rhodesia may contain several % of carbonate impurity. The method of choice follows.

**Alkalies.** Alkalies are determined by the Smith extraction procedure followed by flame photometry. If a flame photometer is not available, the alkalies must be separated and determined gravimetrically by suitable techniques.

**Determination of Traces.** Organic matter is determined by extracting a very large sample of the original asbestos with an appropriate solvent, evaporating to dryness, and drying to constant weight. Magnetite content of chrysotile asbestos varies considerably with the source of the sample. The Arizona asbestos samples contain virtually no magnetite and some Canadian grades (fines or short fibers) may contain as much as 5% or more. For quantitative determination of magnetite, the Shell method may be used. The fluoroborate procedure may also be used but allowances must be made for the solubility of magnetite in the method.

An estimate of the magnetite content can be made by the method described by ASTM for determining the magnetic rating of asbestos used for electrical purposes. Nickel is determined gravimetrically. Chromium is determined colorimetrically.

**Crocidolite and Amosite**
In general, the methods given under chrysotile asbestos may be applied to crocidolite and amosite with little or no change.

Most of the changes involve differences in simple weights or in aliquots taken because of the different levels of concentration of the constituents. For example, chrysotile contains much less iron than crocidolite or amosite. Accordingly, smaller aliquots are used for the total iron determination by potassium permanganate titration. Likewise, a smaller sample size, 0.5 g instead of 1-2 g, is used for determination of iron in crocidolite or amosite. Inspection of Table 2 will aid in the selection of the proper sample size.

**Separation of Manganese.** In the analysis of amosite, manganese must be removed gravimetrically prior to separation of calcium and magnesium. The procedure follows.

**Procedure**

After removal of the R2O3 precipitate, add 5 ml of liquid bromine to the filtrate. Place the solution on a ceramic ring on a steam bath. Overlay with approximately 125 ml of concentrated ammonium hydroxide solution and allow the reaction to proceed slowly for 1 hr. If the reaction becomes too violent, remove from the steam bath and allow to stand for a few minutes at room temperature before replacing on the steam bath. After bromine is entirely expelled, allow the brown manganese dioxide precipitate to coagulate over open steam for approximately 1 hr. Filter using No. 41 Whatman paper or equivalent and wash with 1% ammonium hydroxide solution. Ignite the precipitate in the platinum crucible to 1800°F. Fuse the ignited precipitate with 1-2 g of potassium pyrosulfate. Dissolve the clear melt in 5% nitric acid. Pour the solution into a 100-ml volumetric flask and dilute to volume with water. Use an appropriate aliquot and determine manganese colorimetrically.

**Monitoring and Identification of Airborne Asbestos**

**Introduction**

Airborne asbestos dust is usually monitored for one of three reasons. Firstly, large numbers of samples are taken to check compliance with legislation. As part of the standards issued by most controlling authorities recommended methods are described by which this monitoring should be done. Secondly, within the asbestos industry regular sampling is carried out to determine the efficiency of dust suppression equipment. Here it is frequently necessary to know only the relative amount of dust present, and direct-reading dust monitoring instruments play a key role. Finally, an increasing number of samples are taken for epidemiological purposes. For this it is essential that standard methods be used which can be related to one another, and which remain constant over many years. This work includes monitoring the exposure of people outside the asbestos industry and may involve measuring extremely small amounts of asbestos. The measurement of the airborne fibre number concentration is normally preferred in most countries. This avoids some of the difficulties and uncertainties of mass monitoring by using a microscopical method to separate out only those particles thought to be potentially harmful from a sample of all the dust from the air. The results obtained, however, depend upon the microscopical magnification and technique used and also upon any restriction placed upon the type of particle counted. Some early attempts to monitor the exposure of asbestos workers recorded all the particles thought to be respirable, but most present methods involve counting only those fibres within a limited size and shape range. One advantage of this method is that, unlike the mass standard, the 2 fibres/ cm³ British Standard for chrysotile asbestos (which has been adopted by several other countries), is based upon an epidemiological study. This type of measurement is also likely to provide the basis of any revised standard within the foreseeable future.

**The Membrane Filter Method**

This is now the most widely used method for monitoring asbestos dust in industry. In 1972 a report to the World Health Organization International Agency for Research on Cancer recommended that inter-laboratory trials be carried out, so that this method could be standardized.

(i) **Outline technique**
Measurements are taken by drawing a known volume of air through a membrane filter. This filter is then made transparent, and the number of fibres fitting a standard definition of size and shape which are in the deposit are counted using a phase-contrast microscope. The mean fibre concentration during the sampling period can be calculated. Where fibre identification is needed, different types of sampling filters and analytical techniques may be required.

(ii) Definition of the Fibres which are evaluated
The membrane filter method was developed by the British Asbestosis Research Council in order to try to monitor only those fibres thought to be capable of causing lung damage. At the time of its inception, asbestos or ferruginous bodies were thought to play a major role in the development of asbestosis. These bodies are fibres surrounded by protein and iron frequently found in the sputum of asbestos workers. These fibres are normally longer than 10mm and it was therefore concluded that it was necessary to evaluate only the longer fibres.

(iii) The membrane filter
Cellulose ester filters are normally used for asbestos fibre monitoring. The Asbestosis Research council in the U.K. recommends the use of 0.8-5.0 mm pore size filters, whereas the Australian code of practice suggests that only a pore size of 0.8 mm should be used. Although many asbestos fibres have diameters much less than this, they are in fact captured by the filter and the optical fibre count is not affected by penetration.

(iv) Sampling
The filter is placed in a holder, where it is supported by a gauze or thick pad, which helps in controlling the distribution of air through the filter. The 25 mm Gelman holder is normally used with the filter surface completely exposed. The 37-mm Millipore holder can also be used in this way, or alternatively the face cap may be left in place and the small plug removed.

(v) Transportation of filters
Once the sample has been taken, the open end of the filter holder should be covered with a cap to prevent contamination, and the filter removed and mounted in a clean atmosphere away from the sampling environment. Some codes of practice suggest that the dust deposit should be fixed on the membrane surface while the filter is in the sampling head. Two methods are described.

(vi) Mounting of the filter
The filter must now be made transparent so as to enable the sample to be examined by transmission optical microscopy. Most filter samples are mounted on standard 25×76 mm microscope slides. The 25-mm filters can be mounted whole, but the larger 37-mm diameter filters must be divided into sectors.

(vii) Microscopical Evaluation
Although the filter is now transparent, many of the fibres themselves cannot be seen when using a normal transmission optical microscope, because the refractive index of the background medium is very close to that of the asbestos. The effect is therefore equivalent to looking for a glass needle in a tank of water, and very few fibres are visible. The light which passes through the fibre, however, has a small change of phase relative to that which goes through the background alone.

(viii) Accuracy of the membrane filter method
Errors can occur both in sampling and evaluating the dust samples. Sampling differences are difficult to determine as it is not possible to maintain stable standard dust clouds. The errors are probably similar to those found when sampling spherical dust, and similar precautions should be taken, e.g. the use of isokinetic sampling heads in high-velocity air streams. The effects of electrostatic charges, filter pore size, and sampling flow-rate are not yet fully understood, however. These errors, on the other hand, are probably small compared with those in the microscopical evaluation.

(ix) Recent developments in fibre evaluation
Microscope counting of fibres is not only prone to error, but is also very tedious and time consuming. Methods have therefore been developed either to try to aid the microscopist, or to automate the procedure. Statistical methods have been used to try to reduce the time required to count a slide.

Determination of very low asbestos concentrations

Pathological evidence accumulated over the past decade indicates that asbestos is found in the lungs of most city dwellers and the need to measure the concentration in the general environment has therefore arisen. The methods described so far are unable to monitor accurately the extremely small amount of asbestos present. In order to obtain sufficient fibres for analysis, the dust must be collected from very large volumes of air. Asbestos, however, constitutes only a very small proportion of the particulate matter present, and any fibres present will be obscured by other material.

Alternatives to Asbestos in Industrial Applications

The numerous applications of asbestos are a consequence of its desirable physical and chemical properties, combined with a low material cost. It is this unique combination that makes the replacement of asbestos very difficult in many applications. Some of the properties of asbestos are summarized in Table 2, together with the comparable properties of some of the synthetic fibre materials that have been suggested as replacements for asbestos in some applications. Some of these properties require further comment.

(i) Thermal properties
(ii) Mechanical properties
(iii) Other properties
(iv) Price and availability
(v) Applications

Industrial Applications of asbestos products

(i) Asbestos textiles
Chrysotile fibre forms the basic raw material for almost all of the activities of the asbestos textile industry. The length of flexibility of the longer grades of chrysotile are such that spinning into yarn and cloth weaving are possible. Two basic types of yarn are produced: plain, possibly braced with an organic fibre; and reinforced, which incorporate either wire or another yarn such as nylon, cotton, or polyester. The wire-reinforced yarns and textiles can retain their mechanical properties at temperatures up to 600°C. Recently developed textiles combined with resins and ceramic binders have successfully withstood short-term exposure to temperatures up to 2200°C. The main applications of asbestos textiles are represented in Figure 1. Some of the applications and their alternatives are considered in other sections as indicated.

(ii) Thermal insulations and high-temperature applications
The use of asbestos for insulation purposes encompasses three main areas: asbestos insulation board, asbestos spray, and asbestos for lagging in high-temperature applications. For most high-temperature insulation applications chrysotile fibre is the basic constituent because it combines the properties of resilience, strength as a reinforcement, flexibility, and heat resistance. In some cases amosite fibres are used, such as in the shaped block-type lagging that can be applied to high-temperature pipes, in which a lime/silica binder is used.

(i). 1 Dry asbestos packings
(ii). 2 Asbestos jointings
(ii). 3 Gaskets
(ii). 4 Linings and insulating blocks
(ii). 5 Ceramic and mineral fibres

(iii) Asbestos millboard
(iv) Industrial applications of asbestos-cement
Health hazards of substitute materials

If it is required to replace asbestos on health grounds, then it is sensible to ascertain whether or not the suggested replacement itself constitutes a health hazard. Some of the suggested synthetic fibres replacements for asbestos in specific applications are listed in Table 2 with details of fibre lengths and diameters.

With these observations in mind, examination of the fibre diameters in Table 2 suggests that the various synthetic refractory type fibrous materials that can be used to substitute for asbestos in elevated temperature applications may themselves constitute a health hazard. A mean fibre diameter in the range 2-3mm is quoted for all of these fibres, suggesting that a significant proportion of them have diameters less than the 2mm level thought to be significant in the production of asbestosis.

Studies have also been performed on vermiculite that suggests that it has no tendency towards carcinogenicity or the production of fibrosis in the lungs.

Expanded Perlite can generate airborne dust. This has been examined as a possible health hazard, and is thought to cause no problem, except for nuisance. Experience in the U.S.A. going back nearly 30 years has indicated no related disease pattern with the use of Perlite.

Asbestos-Cement Products

Asbestos-cement products have become well established in industrial and domestic applications. Siding and roofing shingles are manufactured in many attractive colors and designs. Pressure pipe is used in water distribution systems in many municipalities and in industry for conveying water, process liquids, and slurries. The non-pressure pipe is installed in sewage collection systems both in main trunk lines and laterals.

Methods of Manufacture

Asbestos-cement products are manufactured by two different processes, normal and steam cure. A normal-cured product is made with Portland cement and water and is reinforced with one or more varieties of asbestos fiber, usually only chrysotile. The manufactured product is prepared for use by exposure to specified humidity conditions for curing or setting the Portland cement.

The steam-cured product is composed of Portland cement, silica flour (quartz), and water, and is also reinforced by one or more varieties of asbestos fiber. Before use this type of product is both precured and autoclaved at prescribed conditions of time and temperature. The hydrothermal reactions resulting from the autoclaving produce a product which is stronger, more resistant to aggressive agents, and dimensionally more stable. Susceptibility to efflorescence and color fading are also diminished by steam curing.

The normal-cured product is more alkaline because of the unreacted lime remaining from the hydration of the Portland cement. In steam curing, the lime reacts with the silica to form a calcium silicate gel which in turn improves the binder characteristics and chemical resistance of the product.

Normal-Cured Products (Short Procedure). If time is a factor in obtaining analysis required for composition calculations, the following shortened procedure can be used for normal-cure chrysotile-Portland cement formulations.

Procedure

Fuse 1,000 g of a finely ground sample with 5 g of sodium carbonate in a platinum crucible. Digest the clear melt in 50 ml of 1:2 hydrochloric acid in a 250-ml beaker. Disintegrate all siliceous lumps and examine for evidence of any incomplete fusion. When the sample is completely digested, add 6 drops of bromine water and boil to destroy excess bromine and then neutralize using 1:1 ammonium hydroxide with 1-2 drops of methyl red indicator. If the indicator color fades rapidly, excess bromine has not been destroyed.
Transfer the neutralized sample to a 1-liter flask, adjust to the volume with water, and mix well. Let the precipitate settle. The precipitate is a combination of silica and R2O3. Pipet two 50-ml aliquots of the supernatant liquid into separate 250-ml Erlenmeyer flasks. Proceed with EDTA titrations of calcium and magnesium as outlined in analysis of these elements for chrysotile asbestos. If experienced with EDTA titrations, known mixtures of calcium and magnesium should be titrated to recognize the end points. Attention to pH recommendations is important. See asbestos. Calculate the % calcium oxide and % magnesium oxide as follows:

**Use of Additional Fibers in Asbestos-Cement Products.** Calculation of the composition of asbestos-cement products can be complicated by the use of an additional fiber, crocidolite (blue), amosite asbestos, or wood fiber. If these asbestos fibers are encountered, the only analytical approach would be based on the iron content. Both amosite and crocidolite have approximately 40% iron as Fe2O3. If the iron content of the remaining furnish can be estimated, the balance is attributed to amosite or crocidolite asbestos. If the fiber blend is known, the amount of the second fiber can be determined based on the calculated chrysotile value.

**Wood Fiber in Asbestos–Cement Products.** Wood fiber in asbestos-cement products may be determined by wet oxidation of organic matter by chromic acid, absorption, and weighing of the carbon dioxide formed, and correction for the carbon dioxide from inorganic carbonates.

Non-Occupational Asbestos Emissions and Exposures

The most significant exposures of humans to asbestos occur in the workplace. However, persons not employed in asbestos-related occupations are also exposed to asbestos fibres that originate from natural sources or from man-created sources such as the manufacture and use of asbestos products. Such asbestos may be inhaled-as, for example, in an office building in which the air is contaminated by asbestos insulation-or it may be ingested with water, food, and drugs (or, inadvertently, parenterally inoculated). These exposures, termed ‘non-occupational’, are the subject of this chapter.

**Asbestos emissions from natural sources**

The geographic distribution of ultrabasic and metamorphic rock formations in the United States that could possibly contain asbestos is shown in Figure 1. It can be seen that the primary areas of source rock are Minnesota, New England, and many of the Western and Southeastern states (especially in the vicinity of the Appalachian Mountains). Because of high population density, the most critical areas for emissions from natural sources appear to be Eastern Pennsylvania, Southeastern New York, Southwestern Connecticut, and greater Los Angeles and San Francisco.

**Asbestos emissions from human-created sources**

Human-created sources of non-occupational exposures to asbestos include the mining and milling of asbestos, the transportation of asbestos materials and products, the manufacture, installation, use, and demolition of asbestos products, and the disposal of wastes.

**Redistribution and fate of asbestos in the environment**

Because asbestos is exceptionally resistant to thermal and chemical degradation, it persists in the environment and can be widely redistributed by both natural forces and human means. The magnitude of this redistribution is governed by an extraordinary complex set of factors which include the height of the emission source, the rates of air and water flow, fibre diameter, rain, thermal air inversions, electrostatic forces, agglomeration of particles, and the density of vehicular traffic on asbestos-containing landfill, to name only a few.

(i) Redistribution by air

(ii) Redistribution by water

(iii) Ultimate fate of asbestos fibres

**Exposure to airborne asbestos**

As one would expect, airborne asbestos can be found in the vicinity of asbestos mines, mills, manufacturing
facilities, and waste dumps. However, elevated levels may also be found near concentration of braking vehicles, in buildings in which asbestos spray products have been used, and in the cars and homes of asbestos workers who have contaminated them with dust brought from the work area on clothing, body, or equipment. Asbestos may be inhaled by persons who install their own asbestos roofing or flooring, or who repair such items as automobile brakes and clutches, home hearing and plumbing systems, wires for toasters and waffle irons, or the walls of their homes.

Cements, Mortars and Concrete
Cement, in its general sense, is a substance that joins or bonds materials. Hydraulic cement refers to a material that will harden under water and is capable of uniting particles or masses of other solid matter into a compact whole. For the purposes of this article, discussion will usually be limited to hydraulic cements, and will generally refer only to those cements whose strength is achieved through the formation of various calcium silicate and aluminate hydrates. In the United States most of the hydraulic cement used in construction is Portland cement. The analytical methods given were developed primarily for Portland cement, but may generally be applied to the other hydraulic cements.

Hydraulic Cements
Since the early use of lime mortars by the Greeks and Romans, the production of cementitious material has played an important role in the development civilization. The invention of Portland cement, probably by Aspdin in 1824, and the subsequent development of modern concrete led to a present world cement production rate of about two and a half billion barrels a year. In the United States, the rate is now over four hundred million barrels a year, over 90% of which is Portland cement.

Gypsum plasters are produced by the partial or complete dehydration of gypsum, usually to the plaster of Paris or hemihydrate stage. They often contain added accelerators, retarders, and workability agents. Gypsum plasters are distinguished by their low cost, workability and expansion upon setting. Gypsum plaster is not usually considered to be a cement, and this article does not cover the usual analytical chemistry and properties of such a material; see gypsum.

Masonry cements consist of ground mixtures of a cementitious material, usually Portland cement, and hydrated lime, slag, and limestone, or other fillers. Often organic water proofing agents such as calcium stearate and air entrainers, such as sodium abietate, are added. Masonry cements are used for mortars, and as such are characterized by their plasticity or workability and their water retention.

Determination of Compound Composition
Individual hydraulic cements can be identified by determination of their compound compositions, generally through the use of an x-ray diffractometer or a petrographic microscope. Such analysis are seldom required, but the reader who is confronted with this task will find helpful the microscopic data on cement compounds given below or the x-ray and microscopic data given by Taylor or Yang an x-ray pattern of a typical Portland cement. The less complete x-ray data in Lea and Desch may also prove of value. Powder immersion preparations and thin section techniques are used with the petrographic microscope. A micrograph of a thin section of Portland cement clinker . For examinations by incident light, polished sections etched with a suitable reagent that will differentiate compounds present are convenient. Etchants commonly used are dilute solutions of nitric acid, which attack the silicates, and potassium hydroxide, which attacks the aluminates. A very practical etchant is water, of a pH between 6.8 and 7.0, which attacks differently. The ferrite phase has the brightest reflectance and is readily identifiable.

Determination of major components
The chemical and physical properties of most cements have been reported to be almost entirely due to the major components of the cements. The analytical chemistry of cement has thus been concerned primarily with those elements present in major amounts. Recent investigation, however, indicates that some elements present in trace qualities in cement may have important effects out of proportion to their
concentrations.
The procedures given below, applicable to the more common hydraulic cements are capable of producing
great accuracy for the elements or oxides described, provided that the effect of the more common
interferences are recognized. Usual interferences caused by the presence of trace or rare elements, or by
application of these methods to unusual products, can only be detected by analyzing each precipitate
spectrochemically.

**Silicon Dioxide.** Silica can best be determined by gravimetric, colorimetric, or x-ray spectrographic
methods. A method for the determination of free silica is available. The gravimetric method is the referee
method and is described in detail below. The molybdic acid colorimetric is included as part of the rapid
procedure scheme.

**Procedure**
Weigh 0.5000g of the sample into a 100-ml platinum evaporating dish. Add 10 ml of cold water and swirl to
disperse the solids in the water. While still swirling the sample, add 10 ml of concentrated hydrochloric acid.
Warm the platinum dish on a steam bath until solution is complete. Any lumps remaining should be broken
up by using a rubber-tipped policeman. Evaporate the solution to dryness on a steam bath. Remove the
dish from the steam bath and cool.
The difference between this weight and weight of the crucible plus the ignited silicon dioxide previously
obtained represents the amount of silicon dioxide present in the sample. Calculate % silicon dioxide to the
nearest 0.01% by multiplying the weight, in g, of silicon dioxide, less the weight of the blank by 200.

**Ferric Oxide.** Iron, in its oxidized forms, is usually determined by volumetric or colorimetric methods.
Methods for metallic iron and ferrous iron are available. Titration with potassium dichromate is the classical
procedure for ferric oxide and is described below. A colorimetric method is given in the rapid procedure
scheme.

**Calcium Oxide.** Calcium, as determined by the usual gravimetric methods, generally includes strontium. A
given weight of strontium oxide in the final ignited precipitate would be reported as the same weight of
calcium oxide. It is believed that manganese, if not separated prior to the precipitation of calcium,
contaminates the precipitate and leads to slightly high results. There have been some reports in the
literature that do not support this belief.

**Magnesium Oxide.** Magnesium can be determined by gravimetric and EDTA complexometric titration
methods. Flame photometric and atomic absorption techniques are also applicable.

**Titanium Dioxide.** Titanium is best determined by colorimetric procedures such as the one described
below. Some cements may have quantities of vanadium sufficient to interfere with the colorimetric
determination of titanium. Blaine et al.found that less than 5% of nearly 100 portland cements contained as
much as 0.1% vanadium. Slag or portland blast-furnace slag cements, however, may contain appreciable
amounts of vanadium. When its presence is suspected, a sodium carbonate fusion is used to remove
vanadium.

**Rapid Procedures for Major Components**
For product control purposes, a cement plant chemist often requires an analysis of the raw mix, clinker, or
cement as soon as possible after sampling. Classical gravimetric methods for cement analysis are time
consuming. Even when accuracy reducing short cuts are used, such methods require 4 hr or more to
complete. Spectrophotometric (colorimetric) and complexometric titration methods, as recently developed,
permit more rapid analyses.

Colorimetric methods for determining the major oxides in cement and silicates were used by Hedin in 1947.
Since then a number of other investigators have described rapid methods for the analysis of cement,
silicate rock, and related material. Davis gives detailed procedures for the complete analysis (major and
minor oxides) of cements, raw mix, and related material, using colorimetric and complexometric titration
determination of physical properties

Fineness. A finely ground cement hydrates quickly and gains strength faster than a coarse cement of the same chemical composition. Primarily, because of the demand by the construction industry for concrete with great early strength, there has been a trend toward the production of increasingly finer cements. Fineness may be measured by sieving the cement through exceptionally small sieves by the Wagner turbidimeter or by air permeability procedures.

Although a sieve analysis for portland cement is seldom required, the amount of material passing a certain sieve may be a part of specification for other cements. A specific procedure may be required for acceptance purposes, but normal sieving procedures, carefully carried out, generally give equivalent information.

Normal Consistency. Paste and mortar properties, such as strength and time of set, depend on the consistency, or plasticity, of the mixture. The consistency in turn is a function of the water content of the paste or mortar and will vary between cements. A consistency test of a paste or mortar is made to determine the water requirements of a particular cement and, in addition, to provide a neat cement paste, or a mortar, of a desired consistency so that it can be used to cast test specimens for time of set, strength, and air content determinations.

False Set. As cement paste sets, or hardens, it stiffens slowly from a liquid slurry form to one of rock hardness. The rate at which a cement hardens is usually controlled at the cement mill by adding an appropriate % gypsum to the cement clinker during the final grinding of the cement. Infrequently, the % of gypsum admixture is incorrect for a particular purpose, or the cement has been ground at too high a temperature. This can cause the concrete to stiffen prematurely, complicating placing and consolidation of the concrete. Test procedures have been devised to detect and evaluate premature stiffening, or false setting, of cement pastes and mortars. False setting is an abnormal cement property that can be corrected in manufacture or controlled by appropriate adjustments of the mixing period for concrete.

Time of Setting. Problems similar to those associated with false setting are encountered if the normal setting time of a nonfalse setting cement is too short. Ideally, the cement paste should undergo little stiffening during the first hour or so after mixing so that the concrete can be placed and compacted without using an undesirably large proportion of mix water, since excess mix water weakens concrete and decreases its durability.

The setting time of a cement paste depends upon the original water-cement ratio of the paste, the paste temperature, and the drying conditions to which the paste is exposed. Therefore, all times of set are run on pastes of normal consistency, using closely controlled temperature and humidity conditions.

Tensile and Compressive Strengths. The strength of the cement component is a factor affecting the strength of a concrete structure made with the cement. Concrete strength depends upon cohesion between cement grains, strength of aggregates, and adhesion between particles of cement and aggregate. Job specifications nearly always include strength requirements for both the cement and the concrete. Ordinarily, however, the strength of a neat cement paste is not determined. Instead, to compensate somewhat for the strength effects caused by aggregates, mortars incorporating the cement and a standard silica sand aggregate are tested for tensile and compressive strengths.

Soundness. Construction materials made with portland cement should ideally be dimensionally stable once the cement has hardened. Actually, a small amount of shrinkage with some resultant microcracking is virtually unavoidable. It is, however, accommodated by appropriate construction procedures involving proper placement and spacing of contraction joints. Normally the tendency of a concrete to expand after setting is undesirable.

Heat of Hydration. The reaction between cement and water is exothermic. The heat generated by the
hydrating cement in a concrete specimen that is being cured adiabatically may increase the concrete temperature by nearly 50°C. However, a cement’s heat of hydration is usually of concern only in mass structures such as bridge piers or dams, which are too large to permit the heat to escape quickly from the concrete.

**Air Content.** Organic additives to cement may act as foaming agents and cause, during the mixing process, the formation of appreciable volumes of small air bubbles in the concrete. Proprietary organic aids to cement grinding, for example, can entrain such air in concrete. The presence of excessive entrained air will decrease concrete strength.

Raw Materials, Additives and Fuels for Cement

1. **Raw Materials for Making Cement**
   Different types of Cements and their properties were seen. Cement concrete is ‘synthetic rock’ made up by processing raw materials like limestone, clayey materials and ferrugineous materials in proportions that would yield clinker of suitable quality – after going through processes like calcining and sintering.

2. ** Constituents of Raw Mix and their proportioning**
   As mentioned above, limestone, and clay, sand and iron ore or laterite are usual components of raw materials which when added in suitable proportions and ground produce ‘raw mix’.

3. **Proportioning Constituents**
   How to arrive at these proportions is decided by following certain norms and applying certain yardsticks. These yardsticks are:
   - Hydraulic Modulus or Lime Saturation Factor
   - Silica ratio
   - Alumina ratio

4. **Composition of Clinker**
   Clinker should also have, complex compounds, that are formed during the process of sintering, in certain proportions to obtain desired strengths in cement; they are C3S and C2S and C4AF.
   Free lime in clinker should also be limited to less than 1.5%. Burnability factor is another yardstick which furnishes information on temperatures to be maintained in the burning zone to limit free lime to desired values.

5. **Quality Control**
   Quality Control in manufacture of cement is a highly specialized field and is not the subject of this book. It is touched upon to highlight their impact on design of Plant and machinery in a cement plant.

6. **Blended Cements**
   When making blended cements compositions of fly ash and slag should be known so that in what proportions they could be added to clinker could be worked out to produce Pozzolana and Slag Cements respectively. Up to 65% slag can be added to make slag cement; up to 30% fly ash can be added to make pozzolana cement.

7. **Fuels**
   Fuels supply the heat energy required to make clinker from raw mix. Solid fuels like coals which have ash in proportions varying from 10 to 40% also influence the composition of clinker.

8. **Fuel in Shaft Kilns**
   Shaft kilns require low volatile coals. Presently coke breeze is used as fuel in them. Its volatile content is negligible. Coke breeze is ground with raw materials in suitable proportion. Ground raw meal is made into nodules for feeding shaft kilns.

9. **Fuels for Rotary Kilns**
   Rotary kilns can use all types of fuels – solid i.e., coals, lignite and petcoke; liquid i.e., oil and also gas. Solid fuels are fired in pulverized form. Liquid fuels are atomized and fired through oil burners. They need to
be heated to obtain correct viscosity to facilitate atomization. Gas – commonly natural gas is used – can be fired most easily.

10. Coals as Fuel
Coals vary in principal properties like calorific value and ash content from place to place or even in the same place. They are more difficult to burn and quality of clinker produced needs to be watched closely as ash in coal gets almost wholly absorbed in clinker formed – affecting its composition thereby. As a corollary, to maintain uniform quality of clinker, raw meal composition has to be modified to counteract effect of coal ash.

Processes of Manufacturing of Cement

1. Process of Making Cement
Cement is a good example of developments in manufacturing processes used to make a product, which by itself has not changed much.
Developments in processes of manufacture of cement are reflections of the needs of the periods such as scale of production, product quality and specific consumption of thermal and electrical energy to produce it.

2. Predominance of Wet Process
A developed country like America persisted for a long time (compared to Europe) with the wet process of manufacture of cement because of:

1. Alkaline aggregates that were used in Construction Industry in America.
2. Higher requirements of manpower.

3. Marginal grade Limestone and Froth Flotation
Decades ago even when cement plants were few and high quality limestones were readily available, marginal grade limestones was sought to be used to make cement by ‘enriching’ them. The ‘froth flotation’ process used to enrich limestone, removed silica from limestone and thus increased the carbonate content. This process required ‘slurry’ with moisture content of 36-38%. The slurry was agitated and aerated in cells with additions of doses of chemicals that removed ‘silica’ in a ‘froth’ form.

4. Dry and Semi Dry Processes
Dry process has evolved with time. The first cement was produced by dry process. While cements were produced by dry process. Initially dry process kilns were long kilns with chain systems like wet process kilns. Chains had to be of heat resisting steels.

5. Dry Grinding and Blending
As a corollary two developments became necessary:

1. Drying and Grinding of Raw materials in ‘Dry Grinding’. This was not difficult as coal mills and cement mills were already dry grinding mills. Hence, same ball mills could be used to grind materials dry.
2. Blending Dry – As a result of dry grinding it became necessary to blend dry ground fine powders. Development of ‘fluidization’ techniques resulted in ‘Airmerge blending’ systems – first ‘batch’ systems and then ‘continuous’ systems.

Dry process or semi dry process became a reality after dry blending and pneumatic conveying was developed.

6. Semi Wet Process
Many paper and Fertilizer plants produced calcium carbonate sludge as byproduct. It could be used to make cement with small corrections for composition and fineness.

7. Preheaters
The next stages in development were:

1. Traveling grate preheaters.
2. Suspension Preheaters

8. Clinker Coolers
Clinker coming out of the kiln had to be cooled to temperatures at which it could be handled by the then available conveying equipment like pan, drag chain conveyors and by even belt conveyors.

9. Increase in Size of the Cement Plant – Large Kilns
At this point it was realized that kilns larger than this diameter had shorter brick life and gain in capacity tended to be lost due to lesser number of working days.

10. Calciners
At this juncture another epoch making development – that of ‘calciner’ – took place. Calciner carried out the process of calcination outside the kiln almost up to 90%. The kiln was thus liberated from the task of calcination and hence the same kiln could achieve 2-2 ½ times more production. The total fuel was divided between kiln and calciner; kiln receiving only 40-50% and calciner receiving 60-40%.

11. Technical Collaborations
India had Technical Collaborations with World’s leading Process designers and Machinery Manufacturers of Cement Plants since early Sixties. But rate of transfer of ‘Know how’ was rather slow in the decades of sixties to eighties. After that due to policies of liberalization, the rate of transfer of technology accelerated greatly.

Cements based on Natural and Artificial Pozzolanas
Pozzolanas, or pozzolanic materials, are defined as siliceous and aluminous materials that on their own possess little or no cementitious value, but which will – if present in finely divided form and in the presence of moisture – react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties (ASTM C 619-89).

A variety of natural and artificial materials that differ in their chemical composition, mineralogical nature, and geological origin exhibit pozzolanic properties. Chemically they are rich in SiO₂ and - to a lesser extent in Al₂O₃, both oxides being present as constituents of a reactive (glassy or amorphous) phase. The CaO content of pozzolanic materials is low. Sometimes they may also contain limited amounts of chemically bound water. Some pozzolanic materials may also contain non-pozzolanic constituents side by side with those that are reactive.

Fast-Setting Cements
Pastes made from conventional cements preserve their plasticity for several hours before setting and hardening. Such a plastic stage is necessary so that it is possible to produce a concrete/mortar mix of the desired consistency, transport it to the place where it is to be applied, and compact it after placing. In some special applications, however, cements with very short setting times are required. Examples of such applications are various repair works (repairs of pavements, for example) and emergency measures (such as plugging of leaks to prevent leakage of water or other liquids).

1. Control of Portland Cement setting by the use of chemical admixtures
Some highly alkaline chemicals, such as alkali metal hydroxides, carbonates, silicates, and aluminates, cause of significant shortening of the setting time of Portland cement. They act by increasing the pH of the liquid phase, and thus accelerating the hydration of the tricalcium aluminate present in the cement. If alkali silicates are used, soluble SiO₂ is immediately available to react with the calcium hydroxide formed in the simultaneous hydration of tricalcium silicate, and additional amounts of the C-S-H phase are also formed. At moderate dosage of the additives the resulting strengths are increased, but at high dosages the rapid setting caused by the added alkali silicate results in a more disordered structure and a lower strength.

2. Fast-setting gypsum-free portland cement
Conventional Portland cements contain limited amounts of calcium sulfate (in the form of anhydrite or gypsum), interground with Portland clinker, to control setting. Under these conditions the tricalcium aluminate of the clinker reacts with the sulfate and water, to yield ettringite (Aft phase, C₆Al₃S₃H₆). This phase precipitates at the surface of the cement grain as a thin layer, which does not adversely affect the
3. Fast-setting cements containing the phases C11A7.CAF2 or C12A7
Cements that contain the calcium fluoroaluminate phase (11CaO.7Al2O3.CaF2) in combination with calcium sulfate exhibit a very fast setting and initial strength development, owing to the formation of the ettringite phase. In alite-fluoroaluminate cements the fluoroaluminate is combined with tricalcium silicate, whereas the belite-fluoroaluminate cements dicalcium silicate, but no tricalcium silicate, is present.

4. Fast-setting cements containing the phase tetracalcium trialuminate sulfate.
Cements that contain the phase tetracalcium trialuminate sulfate (C4A3S) in combination with calcium sulfate exhibit fast setting and fast early strength development. Such binders include sulfobelite cement, sulfoalite cement, calcium sulfoaluminate modified Portland cement, and sulfoaluminate cement. The setting and initial strength development are brought about by a rapid formation of ettringite in a reaction between C4A3 and calcium sulfate in these cements.

5. Fast-setting blends of portland cement and calcium aluminate cement
Blends of ordinary Portland cement (OPC) and calcium aluminate cement (CAC) exhibit a very fast setting over a wide range of OPC/CAC ratios. Figure 1 shows a typical example of such behavior, but the exact setting time will also depend strongly on the characteristics of the individual cements employed, and on the water/solid ratio of the mix. After setting, the OPC + CAC blend exhibits rapid strength development, and measurable strength values may be achieved within less than 1 hour. The final strengths, however, are lower than those of either the Portland cement or the calcium aluminate cement alone. Figure 2 shows typical strength development of OPC + CAC as a function of their composition.

6. Fast-setting magnesium phosphate cement
Calcined magnesia (MgO) in combination with diammonium hydrogen phosphate [(NH4)2HPO4] or some other water-soluble phosphates yields a fast-setting binder that sets within minutes and yields measurable strengths within less than half an hour.

7. Fast-setting glass cement
Some glasses in the system CaO-Al2O3-SiO2, if ground to a high fineness, yield cements called glass cements, which exhibit very fast setting and hardening. The main product of hydration in such cements in the hydrogarnet phase. Fast-setting glass cements must have a low SiO2 content, as at higher contents of this oxide strätlingite rather than hydrogarnet is formed in the hydration, and this results in an extension of the setting time. Glass cements yielding the hydrogarnet phase as hydration product exhibit a very short setting time and fast early strength development, but only very moderate strength grows later on.

Special Portland Cements
Portland cements are inorganic binders obtained by grinding to a high fineness Portland clinker alone or – most commonly – in combination with calcium sulfate, acting as a set regulator. The ASTM standard C 219-94 define Portland cement as “a hydraulic cement produced by pulverizing Portland-cement clinker, and usually containing calcium sulfate.” The European standard ENV 197-1 requires for Portland cement a clinker content of 95-100% and a content of “minor additional constituents” of no more than 5%, in addition to limited amounts of calcium sulfate.

Portland clinker is a product of burning a raw mix containing the oxides CaO, SiO2, Al2O3, and Fe2O3 (plus other oxides in smaller amounts) to temperatures of partial melt formation. Under these conditions calcium oxide, originally present in the form of CaCO3, first converts to free CaO and then react with the remaining constituents of the raw mix to yield clinker minerals. The most important phase produced in the burning process, and the one characteristic for Portland clinker, is tricalcium silicate (3CaO.SiO2 or Ca3SiO5, abbreviation C3S). The other main phases present in Portland clinker are dicalcium silicate (2CaOSiO2 or Ca2SiO4, abbreviation C2S) tricalcium aluminate (3CaO.Al2O3 or Ca3Al2O6 abbreviation C3A) and dicalcium ferrite (2CaO.Fe2O3 or Ca2FeO2S, abbreviation C2F).
C3A) and calcium aluminate ferrite [ferrite phase, 2CaO(Al2O3, Fe2O3), abbreviation C2(A,F), sometimes also described as C4AF]. In industrial cements these phases are not present as pure chemical compounds, but contain variable amounts of foreign ions in their crystalline lattices.

Packing of Cement

1. **Packing Cement for Despatches**

Cement is produced in bulk and stored in cement silos or large capacities. It is sent to market in general and to individual customers in bags of specific weight filled in the cement plant. Use of and dispatches of cement in bulk has been common in developed countries but in India it is catching up only now.

Filling cement in bags of specific weight required packing or bagging machines which could pack large quantities accurately. Packing machines were developed to satisfy this need. In developed countries paper bags are being used. In India cheapest and durable and reusable material was jute. Hence till now cement used to be packed in jute bags. Jute has now been replaced by high density polyethylene HDPE.

2. **Packing Machines**

Packing machines were developed to carry out the operation of filling each bag with specific weight with a tolerance of + 0.5%.

Necessity to sew a bag was eliminated by making bags with a self closing valve. Bag to be filled was slipped on a spout of the packing machine. It rested on supports which tilted when bag was full and allowed to slip it off the spout. Pressure of cement closed the valve.

A weighing mechanism similar to a weighing scale with a fixed weight of 50 kgs on one side and the bag being filled on the other side of the arm was used for many years to ensure correct weighing of bags. This mechanism is now replaced by electronic weight scales.

2.1 **Rotary Packing Machines**

In rotary packing machines, spouts were arranged on a rotating bin complete with rests for the bags. Operator slipped bags on successive spouts as they were positioned in front of him for the purpose. Bags got filled as machine turned and dropped at another point. One operator was sufficient for capacities up to 100 tph.

For higher capacities rotating machines with two loading and two dropping off points were developed.

3. **Paper and HDPE/Jute Bags**

There is considerable difference in handling paper bags and jute or polythene bags. Handling is easier and faster with paper bags. There is no spillage. Jute bags are more prone to get stuck and spillage is more.

Automatic bags feeding machines have been developed for paper bags. Either rolls of paper bags or bags in a stack are fed to the packing machine by mechanical pneumatic conveyors.

Packing and dispatching operations with paper bags have been fully automated in developed countries.

Storages of Cement

1. **Storages**

Storages are stocks of materials to be maintained in between one part of the process and another to maintain continuity of operation in the event of a breakdown in a section.

Stocks are maintained of:

1. Raw materials i.e., limestones and additives like clay, iron ore, gypsum and blending materials fly ash and slag.
2. Fuel – Coal/oil
3. Semi Finished product – Clinker
2. Daily requirements of Various Materials
In a large plant of 3000 tpd capacity, the daily consumption/production of various materials.

3. Conventions in Storing various materials

4. Factors Governing Storages
Factors governing storages to be maintained for materials bought from outside would be:
1. The distance over which these items are brought, time taken in processing the order and actual receipt of material at site have to be taken into account.
2. Continuity factor, reliability of sources.
3. Climate or weather factor, like differences in moisture content in dry and wet seasons and necessity to maintain stocks dry.

5. Storages of Semi Finished and Finished products
Factors governing storages of semi finished products and finished products within the plant are:
1. Frequently and duration of break downs in respective sections.
2. Process requirements like blending operations, which influence quantity to be stored.
3. Interruptions in productions for long periods for brick lining of kilns changing and grading of grading media and lining plates, roller liners etc. for ball and vertical mills.

6. Storage in Various Sections

6.1 Quarry
Breakdown of shovel/dumper can cause disruption in supply of stone to crusher; but at least 3 shifts are available per week for maintenance; normally standby units are also provided. Therefore no stock of uncrushed stone is normally maintained.

6.2 Crusher
Crusher breakdown will stop quarrying operations will disrupt milling operations unless there is a stock of crushed stone. Often crushes are far from the plant. Maintenance jobs like changing hammers, liners etc., can take longer than time available per week. Therefore 7 days’s stocks are normally maintained between crusher and raw mill.

6.3 Stacker Reclaimer
Stacker reclaimer system design depends on degree of blending required. It depends on number of layers in the stock pile, which in turn are decided by quantity of stone in stockpiles.

6.4 Raw Mill and Blending
Blending silo does not receive raw meal when raw mill stops. Kiln stops when raw meal is exhausted. Major stoppages of raw mill for change of lining plates, rollers, grading of grinding media can take – 2-3 days or 6-9 shifts (normally such jobs will be ‘planned’ in advance to coincide with stoppage of kiln). However for maintaining running of kiln, raw meal stocks of 2-2½ days are maintained. Continuous blending like stacker reclaimer depends for blending effect on no. of layers formed and broken during extraction.
A continuous blending silo, is never emptied to contain less than 40% of its capacity. This is also a factor which decides size and capacity of raw meal storage.

7. Storage After Expansion
This logic can be applied to other storages also to reduce costs of storages as shown in Table 3.

8. Storage of Coal
Let specific fuel consumption be 750 kcal/kg and useful calorific value of coal be 4500 kcal/kg.

9. Storage of Clinker
Clinker will normally be stored under a covered shed. It is a semi-finished product. Weathering (without getting wet) improves grindability.
It would be advisable to have separate stockpiles of clinker for each kiln. There can however be a common stock pile for under burnt clinker and spill over.

10. Space for storages
Creating storages requires heavy investments also considerable space. In a way it is unproductive investment. Out of it helps ensuring production and sales but indirectly. Therefore it is desirable for keeping down the investment, to keep storages to a minimum. However, it is also not advisable to cut things too fine. Stoppage in production due to lack of storage facilities would cause direct loss of revenue.

Ceramics
Ceramics include a wide variety of inorganic materials having diverse chemical compositions, physical properties, and structures. Many ceramic bodies are derived from rocks and minerals. Traditionally the term ceramic is applied to high-temperature silicates but since World war II most high-temperature, inorganic, nonmetallic materials have been termed ceramics. The American Ceramic Society defines a ceramic as “any of a class of inorganic, nonmetallic products which are subjected to high temperature during manufacture or use. Typically, but not exclusively, a ceramic is a metallic oxide, boride, carbide, or nitride, or a combination or mixture of such materials. High temperature usually means a temperature above barely visible red, about 540oC or 1000oF”.

Abrasives
Many materials classified as ceramics are used as industrial abrasives because of their hardness, toughness, chemical inertness, thermal shock resistance, and low thermal conductivity. Many important abrasives are obtained both in nature and by synthesis. Moreover, many significant natural abrasives have compositions very similar to other ceramic materials, particularly oxides. In accordance with the definition of ceramics, those abrasive materials which may justifiably be classed as ceramics include carbides, diamonds, nitrides, silicides, and certain synthetic oxides. About 45% of bonded abrasive grinding wheels are composites bonded with a ceramic, such as glass or porcelain.

Cements, Lime and Gypsum
Portland cement is produced by sintering a mixture of natural raw materials such as calcium carbonate in the form of limestone or chalk, and aluminum silicate materials such as clay or shale. During sintering, chemical reactions produce nodules or clinkers which are composed principally of calcium silicates and aluminates. A blend of the pulverized clinker and a small amount of gypsum is portland cement. Some cements are mixtures of portland cement with masonry, slag, or pozzolan cements. Other cements include iron ore and bauxite, high-alumina, and magnesium oxychloride cements.

Clay Products, Whitewares, and Porcelains
Ceramic clay products are produced by conditioning, forming, and then firing clay or mixtures containing substantial amounts of clay to form sintered or fused bodies of varying porosity. Often the finished article is covered by a glaze or enamel. Typical clay products are clay refractories, china, pottery, sewer pipe, brick, tile, earthenware, stoneware, and chemical ware.

Enamels and Glazes
Enamels, often termed porcelain enamels, are defined as vitreous or glassy inorganic coatings bonded to metal by fusion at a temperature above 425oC. Glazes, on the other hand, are ceramic coatings, often low-melting silicate glasses, which are fused to ceramic bodies. Thus, enamels and glazes are rather low-melting ceramic coatings and are distinguished primarily by the substrate on which they are applied. Enamels and glazes are usually premelted, quenched, ball-milled into a frit, and mixed into a slurry for application and firing to the metal or ceramic body. Metals and alloys which are commonly used as substrates are iron, steel, and aluminum for various commercial applications and copper, gold, silver, and platinum for jewelry. Typical glazed ceramic ware includes china, pottery, porcelain, chemical and sanitary
Glass and Glass Ceramics

Glass, according to ASTM, is "an inorganic product of fusion which has cooled to a rigid condition without crystallizing". It is not a supercooled liquid. Glass is capable of integrally accommodating many elements of widely differing chemical and physical properties. It is this property of glass which enables it to be precisely "tailored" to a wide variety of applications. Strength, elastic modulus, acoustic attenuation, hardness, rheological properties, thermal expansion, electrical resistivity, dielectric constant, refractive index, transmittance of electromagnetic radiation, photo-sensitivity, photochromaticity, and chemical durability can all be adjusted to meet specific applications.

Refractories

Refractories represent a large family of economically important nonmetallic materials which can withstand high temperatures and corrosive environments. Physical and chemical stability at high temperature is the primary requirement for refractory materials.

The terms acidic, basic, and neutral refractories have had extensive and traditional use. Acidic refractories such as silica, fire clay, zircon, and zirconia are characterized by a high-silica content; basic refractories such as magnesite and dolomite contain substantial amounts of magnesia, lime, or alkaline earths; and neutral refractories such as high alumina, chrome, carbon, and silicon carbide consist of materials which are neither strongly acidic nor basic.

Newer Ceramics

During the past twenty years a wide variety of nonmetallic inorganic substances have been developed with precisely controlled properties for applications in many modern devices. These materials differ from traditional ceramics in that they are often nonsilicate synthetic compounds of moderate to very high purity. The control of the unique properties of these new ceramics is an important and growing branch of ceramic science. Examples of such materials include oxides of aluminum, beryllium, magnesium, tin, uranium, and zirconium; magnetic iron oxides and ferrites, ferroelectric niobates, tantalates, titanates, and zirconates; and borides, carbides, nitrides, and silicides.

Determination of the Chemical Composition

The knowledge of the chemical composition of ceramics is a fundamental guide for their characterization. Although the actual analytical methods—gravimetric, titrimetric, or instrumental—correspond to those discussed at the various elements and compounds, the sampling and sample dissolution of ceramics are unique procedures.

X-Ray Diffraction

With the notable exception of glass, most ceramics are composed of one or more crystalline phases and, accordingly, x-ray diffraction plays an important role even in a cursory examination of these materials. Although some ceramics may involve single crystals, most are made up of polycrystalline aggregates, and powder x-ray techniques are usually employed for identification.

X-ray diffraction patterns of ceramics materials are readily obtained by standard diffractometer, electronic detection techniques, or by x-ray photographic procedures such as the Debye-Scherrer powder camera. Specimen preparation is an extremely important consideration in phase identification in ceramics since very inhomogeneous ceramic bodies are often encountered and many of the polycrystalline aggregates may be composed of grains of varying hardness, density, size and orientation.

Lime and Limestone

Limestone is a naturally occurring rock consisting chiefly of calcium carbonate. It is principally the calcareous remains of organisms. When limestone is heated, it decomposes into calcium oxide, commonly called quicklime, and carbon dioxide. The quicklime reacts with water to form calcium hydroxide. This process is usually referred to as slaking; the product is called hydrated lime or slaked lime. Lime is a
general term applied to quicklime and hydrated lime.

Lime and limestone had been used by the Egyptians as early as 4000 BC in the construction of the pyramids. Many of the other ancient civilizations independently discovered the technique of burning limestone, and a variety of uses for the lime produced.

**Properties**

Since limestone is a naturally occurring material, the chemical composition and physical characteristics of limestone and its products vary considerably. The following discussion is presented to show some of the more common properties.

**Physical Properties.** *Color.* The purer forms are white. The lime usually has considerably less gray or tan color than its parent limestone. Impurities in the limestone can produce colors ranging through red (from iron) to black (from carbonaceous material), including the variegated colors of marble and travertine. *Texture.* Limestone usually has a uniform, fine-grained, crystal structure. However, stone from different deposits varies greatly in crystallite size and porosity. Quicklimes often appear similar to their parent limestones. Hydrated lime are usually fine powders.

*Porosity.* The porosity of massive limestone varies from 0.3 to 12%. Porosity is the percentage of voids in the bulk volume of the stone. Quicklime is usually considerably more porous than its parent limestones. *Crystal Structure.* Limestone is either or rhombohedral or rhombohedral in crystal structure. Quicklime is in the cubic system and the hydrated lime are in the hexagonal system.

*Bulk Density.* The bulk density of limestone ranges from 2.0 to 2.8 g/cm³, of quicklime from 0.77 to 1.1 g/cm³, and hydrated lime from 0.40 to 0.64 g/cm³.

*Hardness. The* hardness, on the Mohs’ scale, for limestone and quicklime is from 2-4 and for hydrated lime is from 2-3.

*Refractive Index.* The index is refraction, $n$ is 1.48-1.69 for limestone, 1.70-1.82 for quicklime, and 1.54-1.58 for hydrated lime.

*Heat of Formation.* The heat of formation, at 25°C, is -151.9 kcal/mole for calcium oxide, -235.80 kcal/mole for calcium hydroxide, and -288.5 kcal/mole for calcium carbonate.

*Solubility.* The solubility of limestone varies with temperature and carbon dioxide constant of the water. At 25°C in water free of carbon dioxide, the solubility of calcite is 0.014 g/liter. Quicklime hydrates in water and then has the same solubility as hydrated lime, which decreases with increasing temperature. The solubility of calcium hydroxide in water at 25°C is 1.6 g/liter.

**Chemical Properties.**

*Reaction with acid.* Lime and limestone are inexpensive neutralizing agents. Limes are more efficient than limestones on a mass basis because 44% of the limestone is carbon dioxide, which is not utilized in the neutralization process. The rate of neutralization depends on the reaction products. For example, in neutralization oxalic acid, the reaction product is calcium oxalate, a relatively insoluble salt, which forms on the surface of the lime or limestone particles and retards further reaction.

*Reaction with silica and alumina.* Quicklime and limestone are used in many applications to react with silica. When the reaction is carried out at high temperatures, it produces fused calcium silicates. In the case of limestone, the carbon dioxide evolved serves to mix the molten mass, as in the manufacture of glass and the refining of metals. When lime is mixed with a pozzolan and water, the reaction can occur at room temperatures. Soil stabilization is an example of lime reacting with silica in clay minerals at normal temperatures.

*Reaction with water and carbon dioxide.* Quicklime reacts with water at a rate which depends on the calcination process: dead-burned lime reacts extremely slowly, soft-burned lime can react violently. When calcined properly, quicklime is an effective desiccant. It can remove about one-third its weight of water from air or organic liquids such as alcohols, hydrocarbons, aldehydes, ketones. Lime reacts with slightly moist
carbon dioxide. This is the process which hardens lime mortars used in buildings. As the carbonation proceeds, however, the reaction product forms a barrier which greatly hinders further reaction.

**Uses**
The uses of lime and limestone are widespread. For example, limestone is used for railroad ballast and poultry grit; quicklime is used in the production of steel and in the production of glass; and hydrated lime is used in mortars for the construction of buildings, and the manufacture of grease.

Different applications have different purity requirements. In metallurgical application, the limestone or quicklime is used as a fluxing agent for the silica present in the ore. If, e.g., the limestone contains 2.5% silica, that silica will recast with about 7% of the remaining limestone. Therefore, about 10% more flux stone by weight would be required in the furnace charge than for a stone free of silica. On the other hand, limestone for the manufacturing of portland cement can have 20% silica and be very desirable if the magnesium constant is low. Material to be used in food or food processing has to meet very low limits on certain impurities such as arsenic, lead, and fluorine.

**Silicon Dioxide.** In many samples of lime and limestone, the value obtained for the percent acid-insoluble is extremely close to the value obtained for silicon dioxide when a very complete analysis is carried out i.e., recovering the silica lost even after two dehydrations, and correcting the acid-insoluble residue for impurities usually compensate each other. The total silicon dioxide in the acid-insoluble residue can be determined by removing the silicon as the tetrafluoride.

**Procedure**
Add 5 ml of water to the weighed residue in the platinum crucible from the determination of acid-insoluble matter. Add 2-3 drops of concentrated sulfuric acid, and at least 5 ml of concentrated hydrofluoric acid; the crucible should be about one-third full. Evaporate to dryness in a fume hood. Ignite the dry residue at 1200°C in a muffle furnace for 5 min, cool, and weigh with the tared lid. The loss in weight represents the silicon dioxide content. Save the ignited residue for the ammonium hydroxide group oxides determination.

**Magnesium Oxide.** In the gravimetric method below, the magnesium is precipitated as ammonium magnesium Orthophosphate. If the oxidation of manganese and precipitation of the ammonium group oxides were not carried out carefully enough, the ignited magnesium pyrophosphate will contain manganous pyrophosphate. It is advisable, therefore, to dissolve the residue in concentrated nitric acid and to check for manganese with sodium bismuthate.

**Procedure**
gravimetric method. Add 150 ml of concentrated nitric acid to the combined filtrates and washing from the calcium oxalate monohydrate precipitation and evaporate to dryness on a steam bath. Add about 5 ml of concentrated hydrochloric acid and 50 ml water; and if a slight residue of silica remains, filter through a Whatman No. 40 or equivalent paper. Transfer the filter paper to a platinum crucible weighed with the lid, char, burn of the carbon, cover the crucible, and ignite in a muffle furnace at 1200°C to constant weight.

Calculate the silicon dioxide content from the loss in weight and correct the previously obtained silicon dioxide value accordingly. Dilute the filtrate and washing (or the unfiltered solution) to about 150 ml and boil. Add 20 ml of a saturated solution of sodium ammonium hydrogen phosphate and continue to boil for several minutes. Cool to room temperature. Add concentrated ammonium hydroxide dropwise, with stirring but without scratching the sides of the beaker, until ammonium magnesium orthophosphate begins to form; then add about 10 ml in excess. Continue stirring for 5 min, cover with a watch glass, and let stand for 12-48 hr (longer when the sample contains less magnesium oxide). Filter through a retentive paper such as Whatman No. 2, and wash moderately with cold 1:20 ammonium hydroxide. Dissolve the precipitate with about 50 ml of hot 1:10 hydrochloric acid, wash the filter paper with 100 ml of hot 1:10 hydrochloric acid, and collect the solution in a 250 ml beaker. Boil the solution and reprecipitate the ammonium magnesium orthophosphate in the same manner as before, except use only 3 ml of the saturated ammonium hydrogen...
phosphate solution and add only 5 ml excess concentrated ammonium hydroxide. Let stand for 12-24 hr. Filter through a Whatman No.42 or equivalent paper and wash with cold 1:20 ammonium hydroxide until the washings, acidified with nitric acid, give no test for chloride ion with a dilute silver nitrate solution. Transfer the filter paper and precipitate to a platinum crucible weighed with the lid, char, and bum off the carbon at as low a temperature as possible with free access of air. Cover the crucible and ignite at 1100°C in a muffle furnace to constant weight. One gram of the resulting magnesium pyrophosphate residue is equivalent to 0.3623 g of magnesium oxide.

**Ferrous Oxide.** Exact or even approximate determinations of ferrous oxide are often impossible in samples which contain carbonaceous matter or manganese dioxide. However, if the amounts are small, acceptable results are obtainable. In limestone samples, the ferrous iron usually is in the form of a carbonate.

**Carbon Dioxide.** The sample is decomposed in hydrochloric acid. The liberated carbon dioxide is swept through the gas conditioning train, is absorbed in Ascarite, and is weighed.

**Sulfur Trioxide.** The usual and adequate method of determining the sulfur trioxide content of limes and limestones is to precipitate the sulfate in the acid-soluble fraction with barium.

**Procedure**

Place a 2-g sample in a 150-ml beaker, add 10 ml of cold water, and stir until all the lumps are broken. Slowly add 15 ml of 1:1 hydrochloric acid, heat until solution is complete, filter through a Whatman No. 40 or equivalent paper, and thoroughly wash the residue with hot water. Collect the filtrate and washings in a 400-ml beaker. Dilute the filtrate and washings to 250 ml with water, heat to boiling, and add dropwise, with vigorous stirring, 10 ml of hot 10% barium chloride solution. Stir for an additional 2 min, cover with a watch glass, and let stand overnight. Filter through a retentive paper such as Whatman No: 42, and wash thoroughly with cold water. Transfer the moist filter paper and precipitate to a platinum crucible weighed with the lid, char, and burn off the carbon. Cover the crucible and ignite in a muffle furnace at about 800°C to constant weight. One gram of the resulting barium sulfate residue is equivalent to 0.343 g of sulfur trioxide.

If the sample contains a considerable amount of silica, it is advisable to treat the ignited barium sulfate residue with sulfuric acid and hydrofluoric acid (see section on silicon dioxide, to remove any silica contamination in the barium sulfate before obtaining the final weight.

**Arsenic.** The arsenic is distilled from the sample as arsine in a conventional arsine generator. The arsine is collected in diethyldithiocarbamate reagent after removing any hydrogen sulfide with lead acetate and is determined colorimetrically. Large amounts of heavy metals tend to slow down the evolution of arsine, but this is not a problem with most limes and limestones.

**Lead.** The lead is concentrated by separation of the Group II sulfides. After dissolving the sulfides, the lead cyanide complex is extracted into diphenylthiocarbazone-chloroform, and its concentration is determined colorimetrically. Ferric ion can interfere; therefore, as a precaution, any ferric ion present is reduced with hydroxylamine prior to the extraction. The greatest source of error is contamination from lead carrying dust and lead adhering to the glassware.

**Sodium Oxide and Potassium Oxide.** The large quantities of calcium present in lime and limestone samples make the determination of sodium and potassium difficult. Acceptable results can be obtained by flame emission spectroscopy if aluminum is added to reduce the interference of the calcium and the standard solutions are prepared to contain the same calcium content as the sample. Greater accuracy can be obtained if the standard solutions also contain the same proportions of sodium and potassium.

**Fluorine.** The fluorine content is determined by steam distilling silicon tetrafluoride from the sample and measuring colorimetrically its bleaching action on alizarin red S dye.

**Total Halides.** Total halides are determined by titration with mercuric nitrate solution using diphenylcarbazone as the indicator and calculated on the basis of equivalent chloride.
Slaking Rate of Quicklime. This test measures the reactivity of the material: high reactivity lime is completely hydrated within 10 min; medium reactivity lime is completely hydrated in 10-20 min; and low reactivity lime is completely hydrated after 20 min.

Glass and Glass Ceramics

Glass is a noncrystalline solid; it is characterized by an absence of long-range order in its atomic structure. Although a definition on the basis of this concept would thus include organic as well as inorganic glasses and the metastable state of a variety of normally crystalline elements and compounds, consideration will be given here only to those glasses of major commercial importance, namely, oxide glasses. Consequently, the definition of the American Society for Testing and Materials that describes glass as “an inorganic product of fusion which has cooled to a rigid condition without crystallizing” is appropriate. Equally applicable, but more descriptive is an alternate definition which states, “a glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance, but which, as the result of having cooled from a fused condition, has attained so high a degree of viscosity as to be, for all practical purposes, rigid.”

Constitution of Glasses

Accounting for the diversity and range of properties and adaptability of glasses and glass-ceramics makeup. Few materials are so diversely constituted. Practically every elements in the Periodic Table can be incorporated into a glass. The majority of the elements actively participate in the structure of glass either as network former, intermediate or modifier. The latter class of elements is ionic and interstitial in the structure, whereas the former classifications are characteristically covalent in nature and combine to form the random network “backbone” structure of glass.

Color is imparted, sometimes unintentionally from batch contaminants, through dissolution of such transition elements as iron, chromium, nickel, cobalt, manganese, vanadium, copper, cerium, and uranium. Oxidation state, coordination number, and the presence of auxiliary elements such as titanium will also alter the color of a particular ion. Black glass is obtained with high concentrations of a combination of manganese and chromium, or relatively high concentrations of lead sulfide, iron sulfide, or cobalt polyselenide. Color is also imparted through controlled nucleation and growth of such species as cadmium sulfoselenide, cadmium selenide, selenium, or metallic crystals, eg, gold, copper, and silver, to colloidal particle size dimension.

There are no industry-wide standardized compositions; glass compositions are usually highly proprietary and traditionally they are specified by properties rather than composition. Nevertheless, it may be useful to classify the commercially important products into the following nine categories: soda-lime, borosilicate, aluminosilicate, opal, colored, optical, lead/barium, and special glasses, and glass-ceramics. Table 2 shows the approximate composition ranges in weight percent for some of the leading members of each category, except optical glasses. The range of optical glass compositions is a field in itself and is indicated in Table 3. Table 4 gives typical compositions of some commercially important glasses and glasses-ceramics. Additional glass compositions are tabulated in the CERAMICS article.

Decomposition. All silicate glasses are decomposed by either acid attack with a mixture of hydrofluoric acid and another mineral acid, or by fusion with sodium carbonate followed by digestion with a mineral acid. The choice of approach is dependent on the elements to be determined and the method. Flame spectroscopy, for example, cannot tolerate alkalies such as are introduced by introduced by fluxes, and perchlorate is the preferred anion. Table 6 summarizes the common elements to be determined in glasses and glass-ceramics and the corresponding usual mode of sample decomposition. Obviously a compromise must be made when preparing the sample for the determination of titanium in a barium-titanium-containing glass, since perchloric acid is optimal for barium glasses and sulfuric acid is best for glasses containing titanium.
Chemical Methods for Individual Constituents

It is evident, considering the great diversity of elemental combinations which may constitute glass materials, that no simple all-embracing classical chemical scheme can be given. However, the procedures given here are applicable to most of the commercial glasses and glass-ceramics, such as might be typified by the compositions shown in Table 2.

Flame Spectroscopy

Flame spectroscopy in its general sense embraces all those optical processes that occur in a flame, including emission from excited atoms, resonance absorbance of monochromatic light by ground-state atoms, and fluorescent emission by suitably irradiated ground-state atoms. The last named phenomenon, utilized in atomic fluorescent spectroscopy, has not yet found practical application to glass analysis and hence will not be considered further. On the other hand, few techniques have had the impact on the analytical technology of a class of materials as have flame emission and atomic absorption spectrometry on the analytical chemistry of glasses and glass-ceramics.

In summary, the flame methods enable the glass analyst, without complex manipulations, to accomplish in a matter of hours what formerly required up to two or three days. Since the usual precision of both methods is of the order of 1 to 2% of the amount present, application of flame spectroscopy to glasses and glass-ceramics is usually limited to the minor (1-20 wt %) and trace (less than 0.1 wt%) constituents.

Improvements in the techniques are continuing, particularly in the area of precision, such that even now, taking special care, a precision as low as = 0.5 relative % can be achieved in special instances.

Emission Spectroscopy

Emission spectroscopy has been employed for many years for both qualitative and quantitative chemical analysis of glass and similar silicate-base materials, such as slags, ores, rocks, soils, and ceramics. Early work on the analysis of glass has been documented by Cooper, by Hegemann and Zoellner, by Waed and Hartley and by Lieberman. One of the principal applications of optical emission spectroscopy to glass and glass-ceramic materials is to provide a preliminary compositional survey prior to more extensive chemical analysis by other techniques.

A spectrochemical pellet-spark technique for nonmetallic specimens, pioneered by Tingle and Matocha, and employing a multichannel photoelectric spectrometer can be adapted for the quantitative analysis of glasses. Two hundred mg of powdered sample (~200 mesh) is mixed with 1.8 g of anhydrous lithium tetraborate ( ) containing cobalt for an internal standard in a plastic vial for 60 sec in a suitable mixer-mill. The sample-flux mixture is transferred to a graphite crucible and placed in a preheated furnace at 950 for 20 min.

Polarography.

The principles, methodology, and scope of applicability of this technique are discussed in polarography and voltammetry. For versatility, selectivity, and speed of analysis, polarography is unsurpassed by the other major electroanalytical techniques. Even in its conventional dc form, this approach enabled Williams et al. to develop selective method for the determination of zinc, cadmium, and lead present in the same sample, and a specific method for antimony Zlotowska has also determined lead and zinc in glass, and Marachevskii have reported the polarographic measurement of microgram amounts of arsenic and antimony in silicate materials after a distillation separation of the halides. Square wave polarography was applied by Noshiro and Sugisaki, who reported the determination of antimony and also the simultaneous determination of tin and zinc.

Spectrophotometry

The useful spectral transmittance range of most glasses is from near 300 nm in the ultraviolet to about 5.0 mm in the infrared. This is illustrated in Figure 7. The curve labeled “Plate” is for a commercial plate glass, and is typical for alkali-lime-silica glass types. Code 1723 is an aluminosilicate glass; the curve for this glass is similar to that for Code 7740 borosilicate glass used in laboratory glassware.
X-Ray Diffraction

X-Ray diffraction patterns of crystalline phases in glasses and glass-ceramics can be readily obtained by standard diffractometer-electron detection techniques or by photographic procedures, for example, with the Debye-Scherrer powder camera. Although x-ray diffraction is commonly thought to apply only to crystalline materials, useful structural information may also be gathered from noncrystalline bodies such as glass. The major distinction between the two types of material is that in crystalline matter long order gives rise to Bragg x-ray scattering, while in glass short range order produces rather diffuse patterns. A comparison of x-ray diffraction patterns from a crystalline glass-ceramic and non-crystalline glass is shown in. The discussion of x-ray diffraction in the ceramics articles applies to glass and glass-ceramics. In addition to the topics covered there, the following information is pertinent.

For high resolution diffraction, a Guinier camera is very useful. A monochromator used in conjunction with this device will eliminate all undesirable x-ray wavelengths except Ka1. Closely spaced diffraction lines often found in glass-ceramics can be readily resolved using a Guinier camera mounted on a fine focus of microfocus x-ray generator.

Microscopy

The optical quality and optical constants of glass, surface topography, fracture morphology, and break sources in glass and glass–ceramics, nucleation and phase separation in glass and glass–ceramics, and the variable microstructural features in glass–ceramics, all can be investigated advantageously by various microscopy techniques. Electron microscopy is discussed and optical microscopy. The application of microscopy to glass and glass–ceramics is covered in the ceramics article, Additional methods and techniques are discussed below.

Specimen Preparation for Microscopic Examination. The scope of microscopic examination of glass and glass–ceramics is extremely broad, ranging from the exploration of gross surface and optical defects at magnifications of 3 to 100 by optical microscopy to transmission electron microscope of nucleation, phase separation, and crystal growth of particles 15–1000 Å in size. Universal methods for sample preparation such as outlined by Insley and Frechette and Chamot and Mason and Thornton and Kay are employed for optical, scanning and transmission electron microscopy observations, respectively.

Electron Microprobe Analysis

In recent years the application of the electron microprobe for glass analysis has been increasingly exploited. Electron microprobe techniques are described in Vol. 1, A review of the application of these techni-ques to glass and ceramic material has been reported by Kane.

The electron microprobe has been utilized to chemically analyze defects, stones, inclusions, and cord in glass, to study ion diffraction in simple glass systems to investigate metal and refractory corrosion by molten glass, to scan ceramic to metal seals to determine structural correlations in silicates with x–ray wavelength shifts and to examine archaeological glass specimens.

Since glass and glass–ceramics are nonporous and reasonably uniform in chemical composition, specimen preparation is often routine. However, complications may arise when exposure of glass effects is required, in which case, cutting and polishing operations can prove to be a major task. Some criteria for satisfactory specimen preparation have been given by Yakowitz.

Glass and glass–ceramics are poor conductors of heat and electrons and a conductive coating should be applied to the polished specimen to prevent surface charge build–up and consequent distortion and deflection of the electron beam. Vacuum evaporated copper, aluminum, or carbon films are usually employed to coat insulator specimens.

analysis of gases in glass

Analysis of Blisters. Gaseous inclusions or bubbles in glass, usually called blisters, seriously affect the optical characteristics of glass and, therefore, are of importance in glass quality considerations. The
gaseous components present can often serve as a means of diagnosing the conditions governing the formation of the blisters, and the value of knowing the composition of the gases present is self-evident. The mass spectrometer analysis of the gases in blisters in glass was pioneered by Todd and an improved sampling technique for the analysis has been reported by Neerman and Bryan. Gas chromatography has also been employed for the analysis of the gases in glass bubbles. Work reported by Bryan indicate that reliable gas analyses can be obtained by gas chromatography, but larger sample volumes are required as compared to the mass spectrometer method.

**Outgassing of Glass.** The gas evolved from glass at temperatures below the softening point is an important characteristic when glass is used as an envelope in vacuum or gas–filled devices. Outgassing of the glass envelope can lead to deterioration of the vacuum, contamination of the gas fill, and possibly harmful effects on the components in the device. The energy required for the outgassing process may be furnished in different ways, depending on the conditions under which the device is used. The principal gases evolved depend on the form of energy supplied; heat produces water; electron bombardment, oxygen; ultraviolet radiation, hydrogen, and thermal neutron bombardment of boron–containing glasses, helium. In addition to the major gases, all these processes produce some carbon oxides and water.

**Permeation of Gases in Glass.** The use of glass in ultra high vacuum systems where pressures in the order of 10^-11 to 10^-12 torr are required, in closed systems which contain radioactive or other dangerous gases, and in storage devices such as might be utilized in outer space, has made the accurate determination of the permeation of gases through glass necessary. Early gas flow measurements were made by monitoring the low–pressure side of pressure gages, such as manometers, Pirani gages, Mc Cleod gages, or ionization gages. More recently, mass spectrometers have been employed to measure the flow of gases for diffusion studies. The advantage of the mass spectrometer is that the gas to be studied can be monitored independently of any other gas in the system. This is particularly useful when, as in the case of diffusion in glasses, the gas flow rates to be measured are of the same order of magnitude as the outgassing rates, especially at high temperatures.

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