# HISTORY OF SLAG CEMENTS

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The term "slag cement" is a very general one that can include many types of materials and combinations. We need only to look through a list of the papers submitted at the 7th International Congress on the Chemistry of Cement (Paris, 1980) to find that blast-furnace slags, basic-oxygen furnace steel slags and magnesium slags are used, or are under investigation for potential applications, in cements, and that both copper and nickel slags can be utilized with cements as pozzolanic materials. "Slag cement" is also used at times to refer to a very specific material, as it is in ASTM Standards C219[1] and C595[2]. In C219, slag cement is defined as a "blend of granulated blast-furnace slag and hydrated lime in which the slag constituent is more than a specified minimum percentage." C595 gives the minimum percentage applicable in that particular specification.

In recent years, "slag cement" has been commonly used to refer to either combinations of Portland cement and ground slag or to the ground slag alone. It is possible at times to find varying opinions as to the proper classification for the latter - cement or mineral admixture.

It is appropriate to establish what slag cements are with respect to coverage by this seminar and by this historical discussion. From an historical standpoint, only the use of iron blast-furnace slag will be covered. While all applications of blast-furnace slag in cement will be mentioned at least briefly, the major emphasis will be on the combinations of Portland cement with the slag (Portland blast-furnace slag cements) and the ground glassy slags that can be used for this application. Most of the discussion throughout the seminar will be concerned with these materials.

## TYPES OF BLAST-FURNACE SLAG AND USES IN CEMENTS

Blast-furnace slag is the non-metallic product produced simultaneously with iron in the blast furnace and consists primariy of silica and alumina from the iron ore combined with calcium and magnesium oxides from the flux materials. It is tapped from the furnace at a temperature near 1500$^{o}$C, and, dependent upon the cooling method used, is converted into one of three basic types of product. All are defined in ASTM CI25[3].

Air-cooled slag is a predominantly crystalline material resulting from solidification in a pit under atmospheric conditions. After cooling, it is dug, crushed, and screened to the desired size. The air-cooled slag has little; or no cementitious properties and is primarily utilized as a mineral aggregate used in all types of construction.

Granulated slag is a glassy, granular product resulting from rapid quenching of the molten slag. Quenching with water is the most common process, but air or combinations of air and water may be used. Dependent upon the slag composition and temperature and the speed of quenching, the granulated slag may vary from a friable, popcorn-like structure to small, sand-size grains resembling a dense glass. The slag glass consists of the same major oxides as does Portland cement (but relative proportions differ considerably), has excellent hydraulic properties, and with a suitable activator sets in a manner similar to Portland cement.

Expanded slag is produced by treating the molten blast-furnace slag with controlled quantities of water, usually less than that used for granulation. The product is more vesicular and lighter in weight than the air-cooled slags. Various pit and machine processes may be used to combine the slag and water. The process used and variations in the amount of water control the cooling rate and can result in products varying from highly crystalline materials resembling an extremely vesicular air-cooled slag to very glassy materials similar to those from granulating processes. A pelletizing process[4], now growing in popularity, produces spherical particles of highly glassy slag. Physical properties and the cementitious characteristics of the expanded slags vary with extent of crystallization, as does the appearance, from those of air-cooled slags to those of granulated slags.

Blast-furnace slag is used in the production of cement or cementitious materials in two basic ways: (a) as a raw material for the manufacture of Portland cement, and (b) glassy slag ground and combined with hydrated lime, gypsum or anhydrite, Portland cement, etc., where the slag is utilized for its inherent cementitious properties.

As a raw material for the manufacture of Portland cement clinker, blast-furnace slag can furnish silica, alumina, magnesia and part of the lime required. Fuel consumption in the kiln is reduced somewhat by use of lime from the slag rather than from limestone, since smaller amounts of calcium carbonate must be calcined to remove the carbon dioxide. All of the types of blast-furnace slag are useful in this application; air-cooled, expanded and granulated. The most commonly used for manufacture of Portland cement are the granulated or glassy slags, probably because of ease in handling and more rapid reactions between the glass and other raw materials than would be the case for crystalline slags[5]. Large tonnages of slag have been used in this application, both here and abroad, and often the statistics on the use of slag in cement manufacture do not distinguish between this and the applications in blended cements. Since the final product is Portland cement, and the slag identity is completely lost, this use as a raw material cannot be considered in the "slag cement" category. However, it is an energy-saving and often economical factor in production of Portland cement clinker.

Blast-furnace slag uses in cements, where it maintains its separate identity and is a cementitious component, are divided by Lea[6] into three categories:

(a) Ground glassy (granulated) slag is mixed with hydrated lime. The slag cement covered by C595 and the French and Belgian Ciments de Laitier a la Chaux are examples of this type.
(b) Glassy slag is ground with dead-burned gypsum or anhydrite with a small addition of Portland cement or lime. These are known as super-sulfated cements.
(c) Ground glassy slag and Portland cement are combined in various proportions. These are the Portland blast-furnace slag cements covered by C595 in the U.S., the German Eisen-portland and Hochofen cements, the French Ciments Portland de Fer, de Haut Forneau, de Latier au Clinker, etc.

Each of these types of slag cements will be discussed in the following sections.

**SLAG CEMENT**

The combinations of ground granulated slag and lime were the earliest cements made from slag. Although authorities do not agree on the date of the first use, it seems certain that the properties of such cements were being studied in France prior to 1800, were used in Germany as early as 1822, and were in commercial production in the 1860's.

Slag cement production began in the U.S. in 1896 and the industry grew rapidly, reaching production of over 500,000 barrels annually soon after 1900[7]. The cement was produced at a number of locations, including Birmingham, Chicago, Youngstown, Sparrows Point and Sharon. It was marketed under a number of names including *Puzzolan* and *Portland.* The first specification for slag cement in the U.S. was prepared by the Corps of Engineers in 1902 and covered *Puzzolan Cement,* made by "grinding together without subsequent calcination granulated blast-furnace slag with slaked lime." By World War I, however, the market for slag cement was almost nonexistent, largely caused by misuse of the material. Slags used were often poorly granulated (perhaps even air-cooled in some cases), accelerators were added in large quantities without regard for long-term effects, and as noted previously it frequently was called Portland cement. Poor performance in many instances even led to actual prohibition of the use of any slag in some cement specifications.

By the early 20's only one plant remained in production in the nation although later another company also began to make a slag cement. These materials were used primarily as masonry cements or blended with Portland cement in concrete - the type of applications stipulated for slag cements (Type S) in C595. Although these uses were quite successful and included applications in construction of dams and highways as a partial replacement for Portland cement, all production ended in 1972. The reason was the inability of the manufacturers to find suitable supplies of granulated slag.

In Europe, the lime-slag cements are still covered by Belgian and French specifications but are seldom produced. Major applications in the past were in sea water and underground foundation works because of the excellent sulfate resistance and good plasticity. The virtual abandonment of production of this type of cement in most countries is attributed by Lea[6] to its sensitivity to deterioration in storage and the low strength in comparison to present-day Portland cements.

## SUPERSULFATED CEMENT

Super-sulfated cements have been produced and used in other countries for more than 50 years. They are covered by standard specifications in many nations including Great Britain, Belgium, France and Germany. U.S. specifications, however, contain no provisions for this type of cement.

The cement is usually made by grinding a mixture of 80-85% granulated slag, 10-15% gypsum or anhydrite and about 5% Portland cement. It possesses outstanding resistance to a variety of aggressive agents: sea water, sulfates, weak acids, chlorides, alkali hydroxides, etc. As a result, super-sulfated cements have been used very successfully in sea water work, concrete pipe exposed to aggressive ground waters, in chemical plants, etc. Strength characteristics of the cements are excellent; they have a low heat of hydration. Compared to Portland cements, they are more susceptible to carbonation during storage, and require extra care during the initial curing period to keep the surface moist, if a friable, dusty layer is to be avoided.

Recent interest has been expressed in the U.S. in super-sulfated cements, probably due to their resistance to seawater and sulfates, which is better than that of other cement types.

## PORTLAND BLAST-FURNACE SLAG CEMENTS

Portland blast-furnace slag cements constitute the most successful and widely used variety of "slag cements" throughout the world. Consisting of a mixture of Portland cement and ground granulated slag, they are subject to many different specifications with respect to strengths and slag contents in the various countries. In most nations, one of the Portland blast-furnace slag cements is intended to be the equivalent of, and meet the same requirements as, ordinary (or Type I) Portland. Others, often with higher slag contents, have special properties such as higher sulfate resistance and lower heat of hydration. In the U.S. these cements are currently covered by C595.

Who "invented" Portland blast-furnace slag cement - and where - is not a matter of agreement by all authorities. There is general concurrence that commercial production of such cement began in Germany in 1892. It was met by a great amount of suspicion and opposition - fears that the sulfides present would cause expansion and corrosion of reinforcement and that it would not have adequate strength development if exposed to air. As a result, early uses were restricted to structures in sea water, foundations, etc.

However, laboratory investigations and field use in many countries have demonstrated that no basis exists for the many suspicions. Lea (6) summarized much of the extensive literature on blast-furnace slag cements with the following general conclusions regarding the product performance.

(a) Blast-furnace slag cements have a long history of successful use in all types of applications.
(b) Strength development is usually slower than Portland cements at early ages with greater strength gains at later ages. Adequate strengths are provided by either rich or lean mixes, in either air or water.
(c) The sulfides disappear without causing any expansion or instability of any kind.
(d) Protection for embedded steel is as good as that of other cements; there should be no objection to their use for reinforced or prestressed structures.
(e) Resistance to freezing-and-thawing is similar to that of Portland cements; the cement, apart from effects on air entrainment and the air void system, is a minor factor.
(f) Portland blast-furnace slag cements are more resistant to sea water and other chemical agents than ordinary Portland cements. While high alumina slags have been reported to decrease sulfate resistance at low percentages of cement replacement, all slags increase the sulfate resistance at high replacement levels (65% or more).
(g) Expansion of concretes made with alkali-reactive aggregates is considerably reduced by use of slag cements as compared to Portland cements with the same alkali content.
(h) Blast-furnace slag and Portland cement can be combined to duplicate the characteristics of any Portland cements except the high early strength products (Type III in the U. S.).
(i) Slag cements may require more careful handling at low temperatures when the rate of strength development is decreased more than with Portland cement.

Although uses of Portland blast-furnace slag cement grew rapidly in Europe, it was not until 1938 that Green Bag Cement Division of Pittsburgh Coke and Chemical Company began its manufacture in the U.S. The first U.S. specification, ASTM C205, was issued in 1946 (now covered as Type IS in C595). In the late 1950's some 12 cement plants of eight different companies were producing this cement.[8] The use of the slag was primarily to increase production during a period of cement shortage; as kiln capacity was increased, the use of slag decreased. The Type IS cement never was larger than about 1½% of the total U. S. cement production and has since decreased to an almost infinitesimal amount. It did establish an excellent service record in many types of work, however.

In contrast, it has been reported that blast furnace slag cement has represented high percentages of total production in many countries in recent years: 24% in West Germany, 32% in Belgium, 42% in France, 55% in the Netherlands, etc.[9] However, many of the cements use a relatively low amount of slag and comparisons of slag use are difficult. In nations where actual information on the amount of slag used has been available (Germany, France and South Africa) it appears that the tonnage of slag ground for use as a cement is equal to about 10% of the total cement tonnage. Similar use in the U.S. would take about 8,000,000 tons of slag annually - nearly 1/3 of the recent production.

Most of the blast-furnace slag cement production has been by inter-grinding the slag and the clinker, although separate grinding is permissible in a number of specifications. It has long been known that the slag is harder to grind than the clinker and inter-grinding leaves the slag coarser than the cement. This is the exact opposite of the desirable situation, which is to have the slower hydrating slag ground the finer. Separate grinding has the basic advantage of permitting the slag and the cement to be ground to their own optimum finenesses. Separate grinding has long been used in Japan and more recently to some extent in France, with the slag and cement then blended prior to delivery to the customer.

Some 20 years ago another improvement was added to the separate grinding in South Africa: separate marketing, with the slag and cement combined in the mixer.[10] This has permitted proportions to be varied to suit the particular job needs. The same procedure was begun in England some 10 years ago and in Canada about 5 years ago. More recently it was started on a smaller scale in the U.S. These operations have demonstrated that such mixtures have better workability and placeability and produce concrete having greater uniformity than do mixtures made with the Portland cement alone.

During the nearly 90 years that Portland blast-furnace slag cements have been produced, many efforts have been directed toward the selection of the slag based on its properties and cementitious characteristics. Procedures developed for identification of the more cementitious slags have been reported in literally hundreds of papers and summarized and evaluated in several.[6,9,11] The systems proposed have included various moduli based on chemical composition, indices determined from mortar tests of slag-cement and silica-cement combinations, determinations of glass content by a variety of methods, and mortar tests using other activators such as NaOH. No single, simple method has yet been developed, although many of the procedures would have considerable value as a quality control aid for specific situations.

Among the factors that determine the performance of a slag in Portland blast-furnace slag cement are the following:

(a) Chemical composition of the slag. The more basic materials may be expected to be more cementitious, assuming other factors to remain the same. However, the amounts of minor components often have a significant effect.
(b) Glass content is important, with high glass content desirable, but large variations in results can be produced by different glass structures, determined to some extent by its thermal history.
(c) Fineness of grind determines the rate of reaction. A single factor such as surface area may be misleading, however, because of differences in the grain size distribution.
(d) The amount of slag used in the blend will, of course, determine the magnitude of modification of the cement characteristics.
(e) Finally, the performance of the slag will be partially dependent upon the chemical composition and fineness of the cement with which it is combined.

Any blast furnace slag having a significant amount of glass and finely ground will have some cementitious characteristics. Determination of its properties, blended with any given cement, is best determined by tests with that cement.

The most recent development that has further increased the value and usefulness of slag cements is the high costs and prospective shortages of energy. The slag does not need to be burned in a kiln. Pointing out that slag is the only cement component other than Portland cement clinker that can be used either as a secondary or main constituent of the cement, Smolczyk[9] summarizes the situation as follows: "In countries where suitable blast-furnace slags and sufficient experience with slag cements are available, blast-furnace slag cements are used in the same way as other cements and in certain cases they are favoured. . . The tendency is increasing for there is no other cement component by which more energy and natural resources can be saved than it is with the granulated blast-furnace slag."

## SUMMARY

A well-known cement research worker once concluded a talk on the use of blast-furnace slag in cement manufacture with these statements:[5]

"But little in the nature of a conclusion can be added to what has been given above, since that is obviously only a summary. Slag had already been blended for a long period with lime at the period when Portland cement commercially was but a curiosity and had but an extremely limited use. It is evident, further, that slag has long been used to blend with Portland cements and in so doing has not deleteriously affected its strength. The long and continued use of such blends abroad would indicate that the consuming public has no doubt regarding its serviceability. What relatively little use has been made of slags blended with other materials in the U.S. has extended over as long a period as has the use of Portland cement, and apparently the expected service has been realized.

It would seem, therefore, that there is the possibility of widely extending the use of blends of slag and other materials in this country, which at the present time seems so anxious to use hydraulic cements other than standard Portland. Although slags have been very extensively used here as a raw material in the manufacture of Portland cement, it is evident that slags need not lose their identity to find a market in the cement field."

We now have another 45 years of experience with slag cements since Bates wrote those conclusions. There have been improved processes developed for production and use of slag in cements. The high cost of energy has made such applications much more attractive economically. It is time to begin a new chapter m the history of slag cements in the United States, by increased use of ground slag combined with Portland cement, using all of the techniques now available.

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