Cement Aging: Something of the Past!

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Abstract

The aging behavior of calcium aluminate cement packed in plastic bags was investigated by storing in a warehouse for 40 months. The cement was tested periodically in a castable for mixing behavior (wet out time), self-flow behavior, setting and strength.

Introduction

Calcium aluminate cement, well established as a binder in the refractory industry, shows hygroscopic behavior and needs to be protected against moisture pick up during the storage period to prevent the cement from aging. The use of aged cement has an impact on the workability and setting behavior of refractory castables.

Multilayer paper bags are commonly used as standard packaging for cement, often in combination with additional pallet protection, e.g. stretch hood or shrink wrap. Nevertheless cement packed in paper bags has a limited shelf life. The guaranteed shelf life provided by the suppliers is typically between six and twelve months.

In the 1990s extended tests were carried out to investigate the shelf life of Almatis calcium aluminate cements. This included Brazilian warehouse storage and even more severe testing under "jungle room" conditions in a climate chamber. Based upon the results of these tests, a shelf life of 12 months is guaranteed in the Almatis calcium aluminate cements datasheets [1], if material is stored under adequate dry conditions.

Offenbecher [2] investigated the influence of bag design and storage conditions on the shelf life of cement. Standard Portland cement originating from the same batch was packed in different types of paper bag, with and without a moisture barrier. For each bag design, one pallet was covered with an additional stretch hood and another pallet had no pallet protection. Each was stored for six months in a dry warehouse. For the evaluation of moisture protection standardized cement quality testing was performed. This shows the impact of moisture on the product properties, e.g. water demand, initial setting and soluble chromate concentration. All bag designs without additional pallet protection show aging effects during storage. Differences in cement properties become significant after two months for the chromate concentration, and after six months for standard consistency and setting time.

Cement in bags without a moisture barrier and any pallet protection also show an increase in water demand. Water demand remains stable for cement packed in bags incorporating a moisture barrier. For pallets which are covered with a stretch hood, the type of bag is of minor importance and cement parameters such as initial setting and water demand remain stable over the entire storage period.

Almatis has alumina production facilities in the different regions but cement production is concentrated at the Rotterdam plant. Cement is shipped from Rotterdam to all regions of the world. For this reason proper packaging is mandatory. Almatis cement is packed in paper bags with a plastic foil within the paper to act as a moisture barrier. All pallets are also shrink-wrapped. However, during intercontinental transport through different climate zones condensation can occur which could cause formation of lumps in the middle of the pallet despite the additional protection as shown in **Figure 1**.

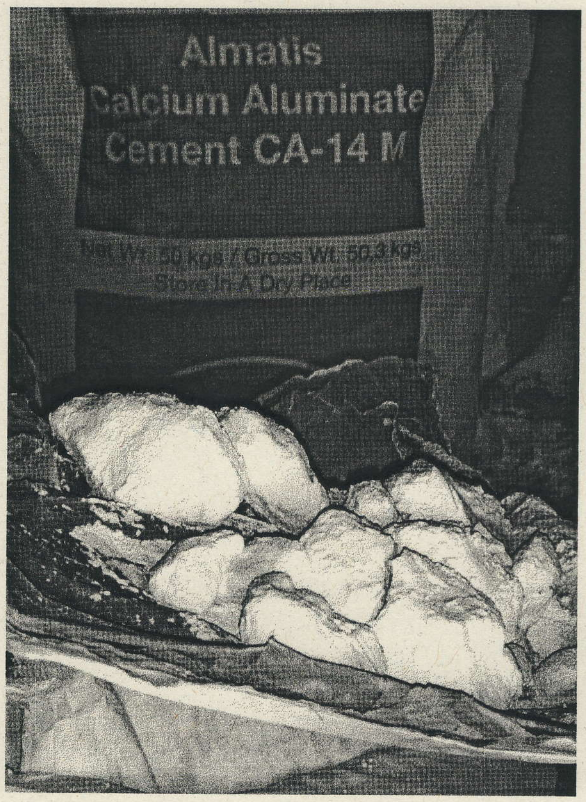

Figure 1. Lump formation during intercontinental transport.

Several options have been considered to further improve the moisture protection for cement packaging for all shipments, and intercontinental shipments in particular. Moisture absorption bags added to the containers are a simple approach but whilst providing protection during shipment, do not provide protection during later warehouse storage. Special refrigerated containers are said to be very effective, but are expensive and also only limit the protection during transportation. Plastic bagging of cement was considered the best approach as it provides full protection from bagging in the plant until the time when the product is finally used. It was expected that the general shelf life problem with cement could be overcome using this solution.

This study presents the results of long term aging testing of calcium aluminate cement, packed in plastic bags (**Figure 2**), which has been stored in a warehouse for up to 40 months. A series of tests were performed using Almatis cement grade CA-470 TI which is the most critical of all Almatis cements when considering moisture absorption.

Test Castable

For shelf life testing of CA-470 TI a low cement self-flow castable based on tabular alumina has been used. It contains dispersing aluminas ADS/W as additives. The castable matrix is composed of T60/T64 -45MY LI and -20MY and reactive alumina CL 370. The water demand was adjusted to 4.9% (**Table I**).

This test castable "Norcast 5" is also used for the quality control of the CA-470 TI in the Almatis laboratory in Rotterdam.

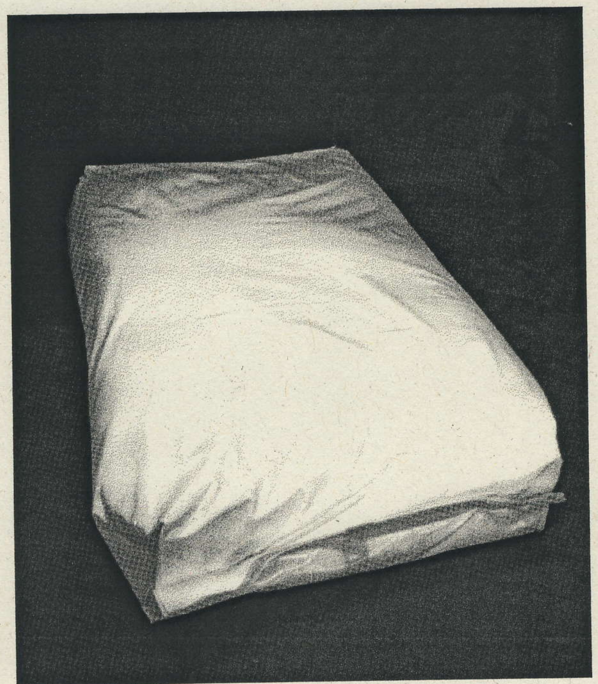

Figure 2. Test plastic bag for Almatis cement.

Test Conditions

Calcium aluminate cement CA-470 TI, produced at the Almatis plant in Rotterdam, was packed in 25 kg sealed plastic bags (figure 2). A pallet of two metric tons from the same batch was shipped to the plant in Ludwigshafen and stored in a warehouse tent for up to 40 months. The bags were protected from rain, but the cement was exposed to seasonal temperature and humidity variations. The pallet was stored without shrink wrap protection.

For comparison a series of tests were also performed with CA-470 TI packed in standard paper bags (multi-layer: paper-plastic foil-paper) and stored under the same conditions for up to 12 months. In addition one plastic bag was stored outdoors at the Rotterdam plant for 12 months after 20 months storage in the warehouse.

Before testing the cement, the particular bags were stored in the lab at 20°C for temperature acclimatization. Within one week the cement was tested in the castable Norcast 5 for wet out time, flow behavior up to 60 minutes, setting and strength after various pre-firing temperatures (**Table I**). A new unopened bag was always used each month and for the particular test period in the lab, the open cement bag was stored in a properly closed vessel.

Table I

Composition and Initial Properties of Self-flowing Test Castable

Component \ Castable			Norcast 5
Coarse fraction T60/T64	3 - 6 mm	%	30
	1 - 3 mm	%	15
	0,5 - 1 mm	%	10
	0,2 - 0,6 mm	%	5
	0 - 0,3 mm	%	10
Fine fraction T60/T64	- 45 MY Li	%	8
	- 20 MY	%	7
Reactive Alumina	CL 370	%	10
Cement	CA-470 TI	%	5
Dispersing Alumina	ADS 3	%	0,8
	ADW 1	%	0,2
Water		%	**4,9**
wet out time		sec	60
self flow	10 min	mm	279
	30 min	mm	274
	60 min	mm	261
EXO	Start 1		138' / 24,1°C
	Start 2		4,8h / 26,0°C
	Max.		6,1h / 31,6°C
ultrasonic setting start		min	112
CMoR	20°C / 24 h	MPa	6
	110°C / 24 h	MPa	15
	1000°C / 5 h	MPa	9
	1500°C / 5 h	MPa	41
CCS	20°C / 24 h	MPa	22
	110°C / 24 h	MPa	82
	1000°C / 5 h	MPa	41
	1500°C / 5 h	MPa	130
Density	110°C / 24 h	g/cm³	3,10
	1000°C / 5 h	g/cm³	3,08
	1500°C / 5 h	g/cm³	3,07
Shrinkage	110°C / 24 h	%	-0,02
	1000°C / 5 h	%	-0,08
	1500°C / 5 h	%	+0,02

The castable was wet mixed in batches of 5 kg using a Hobart A 200 planetary mixer at speed 1 for 4 minutes. The castable properties were tested at a constant water demand. The wet out time was determined as described in a previous paper [3]. The flow properties after 10, 30 and 60 minutes (F10, F30, F60) were measured by the cone test (lower diameter 100 mm, upper diameter 70 mm, height 80 mm). The setting behavior was measured by both exothermic and ultrasonic equipment as described in a previous paper (**Figure 3**) [4].

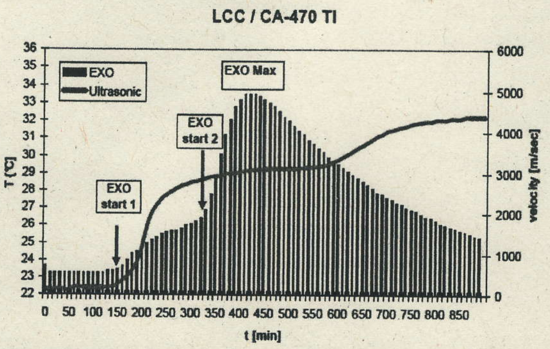

Figure 3. Measurement of setting by exothermic reaction and ultrasonic equipment.

The test period of 40 months can be split into two phases: for the first 21 months the setting occurred in the air conditioned lab at 20°C, whereas for the second phase (22 – 40 months) the samples were put in a temperature cabinet at 20°C. Experience showed that the lab air conditioning was not able to keep the room temperature constant at 20°C, and therefore the change was made.

The test series will continue until the cement becomes unusable or is consumed.

Results and Discussion

In general, the test castable can show some variation in results during the testing period. These are not considered to be due to aging unless the specific values are confirmed by later results. For example, lower flow values were noted after 11 – 13 months, but from 14 – 40 months flow values comparable to the initial results were again achieved.

It has also been accepted that there can be some variation in measurement of setting behavior, both exothermal and ultrasonic, without attributing this to aging unless a clear trend occurs.

The wet out time is about 60 seconds and the flow values at 10 and 30 minutes are on average 280 mm. For cement in plastic bags these values remain stable over the entire test period. This is shown in **Figures 4 and 5**.

The ultrasonic setting start ranges from 72 to 228 minutes without showing a trend towards longer setting (**Figure 6**). The variation range in phase 1 (up to 21 months) is higher when compared to phase 2 (22 – 40 months). The higher variation in phase 1 was the motivation for testing the setting in the temperature cabinet, and indeed phase 2 shows a narrower range of ultrasonic setting start. These results show that even slight temperature differences of a few degrees only can have an impact on the setting start of low cement castables.

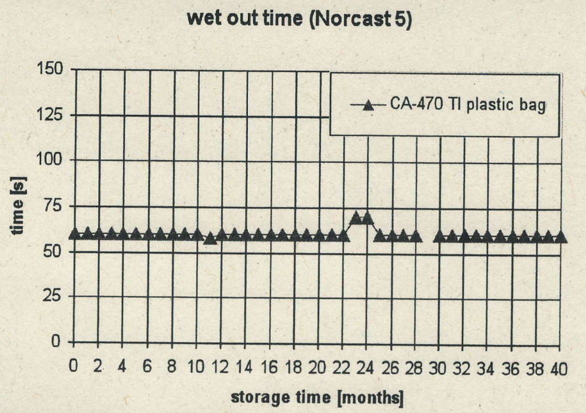

Figure 4. Impact of warehouse aging of plastic bagged CA-470 TI on wet out time. See text regarding data point at 32 months.

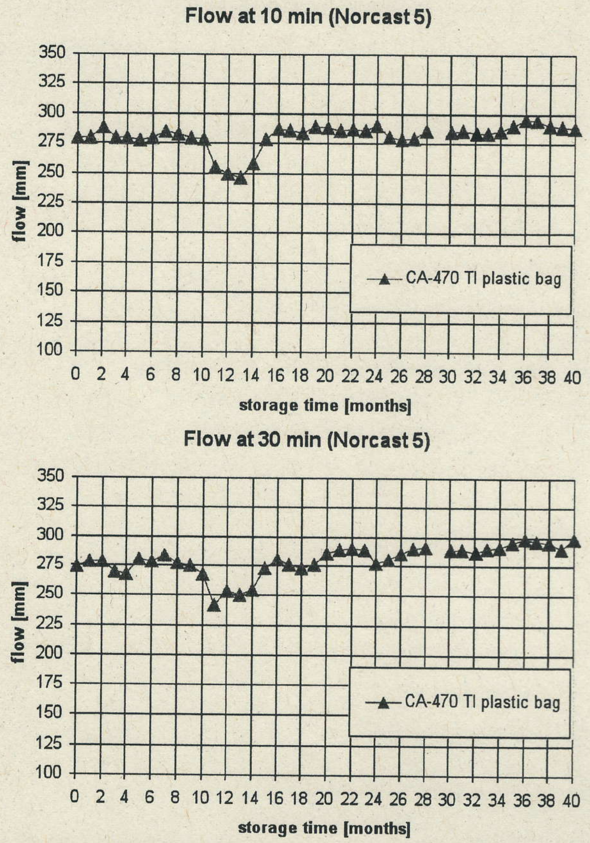

Figure 5. Impact of warehouse aging of plastic bagged CA-470 TI on flow at 10 and 30 minutes. See text regarding data point at 32 months.

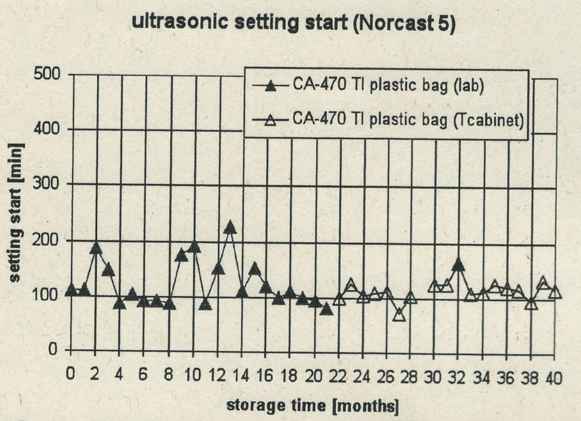

Figure 6. Impact of warehouse aging of plastic bagged CA-470 TI on ultrasonic setting start. Measurement phase 1 (0 – 21 months) in the lab and phase 2 (22 – 40 months) in a temperature cabinet at 20°C. See text regarding data point at 32 months.

The EXO results given in **Figure 7 a-c** also show the effect of tighter temperature control in the temperature cabinet. Here, the variation range of setting start also becomes a bit narrower, and the overall levels of EXO start 2 and EXO MAX show a difference between phases 1 and 2. The setting times increase considerably when setting occurs in the temperature cabinet. Obviously the cabinet is reacting quickly to the temperature increase of the castable during the exothermic cement hydration and can quickly cool the sample back down. This retards the hydration reaction and results in longer times for setting start 2 and EXO Max.

The longer EXO setting times during phase 2 are not related to a cement aging, but are only due to the change in testing conditions. Cement samples aged for 38 to 40 months which were tested under the same conditions as in phase 1 still show the same setting times as the samples tested after aging in the period up to 21 months (**Figure 7 b and c**).

It is unclear as of yet whether the use of a temperature cabinet has an impact on other castable properties. As the temperature development at EXO Max is much lower when the setting occurs in the temperature cabinet at 20°C in comparison to the laboratory at 20°C, it may result in lower strength properties. This is currently being investigated and will be reported later.

The strength data given in **Figures 8 a-d** show some variation but no trend which could be attributed to an aging effect. The strength testing was performed on two test bars, but not multiple samples, at each temperature. This must be considered with regard to the statistical variation which is normal for castable strength testing. Density and permanent linear change values remain very stable over the entire test period.

Calcium aluminate cement CA-470 TI packed in plastic bags shows no aging trend over a storage period of 40 months when tested in test castable Norcast 5. In comparison CA-470 TI packed in paper bags shows a clear aging trend with regard to setting behavior. The exothermal measurement already shows an increase in setting times after two to three months, and a steep rise after five months storage. Then EXO Max is at 1200 minutes when compared to 366 minutes for the fresh cement.

Even the one plastic bag which was stored outside for one year shows no aging trend for wet out, flow or for setting times. The data points for this sample are highlighted in figures 4 – 7. The overall age was 32 months (20 months warehouse plus 12 months outside). Wet out of 60 seconds is achieved and a flow of 287 mm after 30 minutes. Ultrasonic setting shows the start at 164 minutes whereas the first rise in the EXO graph occurs a little later at 186 minutes.

Practical Aspects

In addition to the moisture protection, other features are important for proper cement packaging. The de-aired 25 kg plastic bags are compact and easy to handle. An anti-slip coating on the bag surface prevents the bag from sliding off the pallet during fork lift transportation. The disposal of the plastic bags is not considered as a problem as plastic bagging has in recent years become common practice. In Germany a system called WEPA is in place for returning empty bags.

A new plastic packaging line has been installed in the Rotterdam plant for all Almatis cement grades.

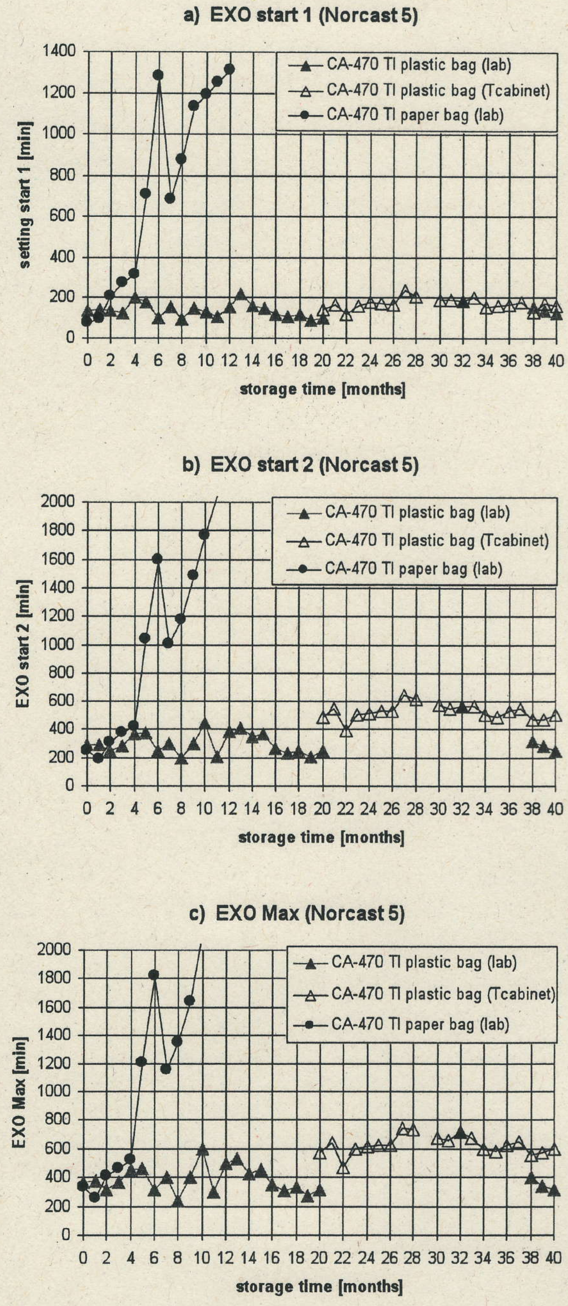

Figure 7 a-c. Impact of warehouse aging of CA-470 TI on setting (EXO start 1, start 2, and Max); plastic vs. paper bag. Measurement for CA-470 TI in plastic bags: phase 1 (0 – 21 months) in the lab and phase 2 (22 – 40 months) in a temperature cabinet at 20°C. See text regarding data point at 32 months.

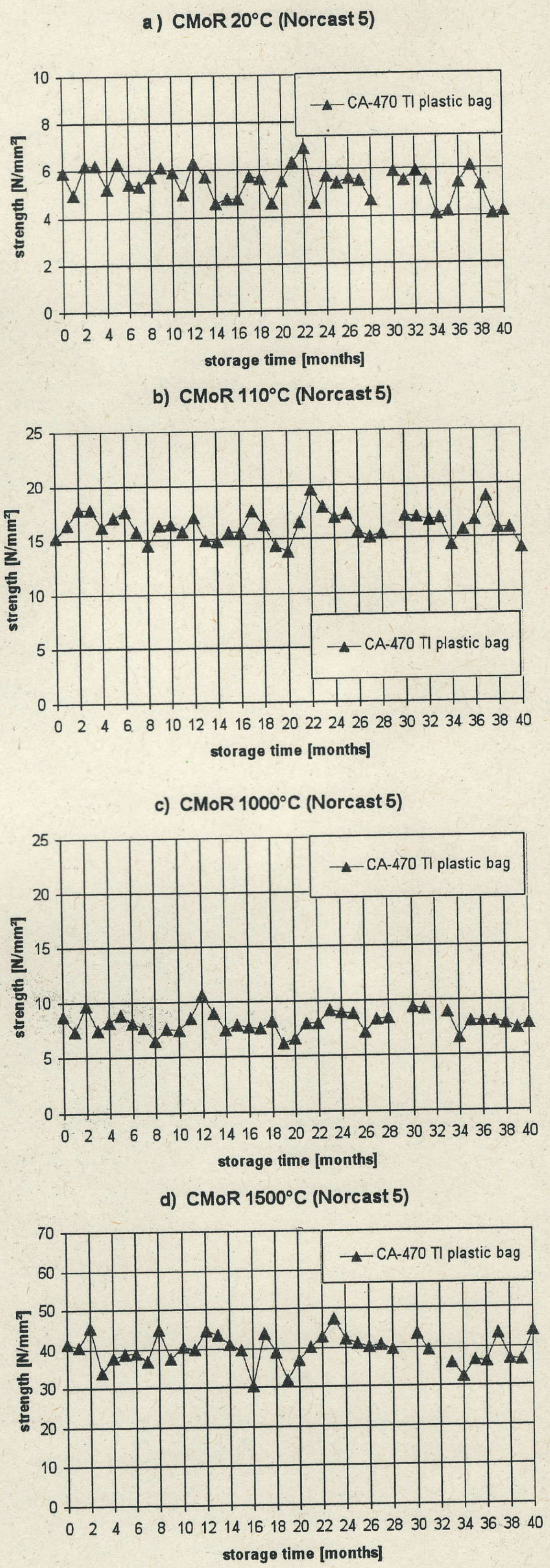

Figure 7 a-c. Impact of warehouse aging of plastic bagged CA-470 TI on strength of test castable (CMoR 20 – 1500 °C). See text regarding data point at 32 months.

Summary

Calcium aluminate cement CA-470 TI packed in plastic bags did not show any aging trend even after a 40 month storage period. The extended tests prove that plastic bags provide a much better moisture protection and preserve the guaranteed properties of the cement for much longer storage times when compared to paper bags. Plastic bags can overcome potential moisture and lump formation problems in overseas shipments and provide a long shelf life even after the pallet shrink wrapping has been removed. Plastic bags are also advantageous when for some reason a pallet is stored outside, or the "first in - first out" principle is not applied and cement is stored for a longer period than usual.

Plastic bagging paves the way for packed cement with greatly extended shelf life. Cement aging: something of the past!

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FUTURE PROGRESS IN THE FIELD OF REFRACTORIES

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Refractories are of such vital importance in the iron and steel industry that any subject matter which tends to increase their service ability to this industry is of interest and value. Consequently, a considerable amount has been written on this subject in a general way. This paper, however, general as it is, directs attention along two avenues, which is believed will lead most directly to the progress that is to take place in the future.

Progress has resulted in all branches of industry as a result of the coordination of knowledge and experience in a systematic or scientific manner. Producers and consumers cooperate to their mutual interests in extending the usefulness of commodities. There has not been developed, however, the cooperation between the manufacturer and user of refractories to affect the progress that is to be desired in this field.

The whole problem of advancement in the utility of refractories is of such a complicated and obscure nature that at times it appears hopeless. The manufacturer or user cannot solve the problem alone and it is only through the closest cooperation and critical study by each group that significant progress can be made.

One of the two means of accomplishing this aim is by interesting the user in the value resulting from his analysis of refractory problems. Provided he will become more familiar with the properties and limitations of refractories and apply this knowledge in a critical study of specific conditions in service, the information gained will be of great value to the consumer and producer as well.

The second means of advancement is through the manufacturer obtaining the service data and developing his material so as to furnish properties that will meet the service conditions to the greatest possible degree.

Progress in either direction will necessarily be slow. One factor is the low cost of refractories per ton of finished material, and consequently consumers may not be as deeply concerned with this problem as with others. Increased efficiency in all branches of industry has, however, had its effect on the refractories used in furnace operations. Years ago fire brick were purchased on the recommendation of the head bricklayer. During this period many of the brick used were found to be satisfactory by reason of the social or business relation between the head bricklayer and the refractories salesman. If brick were tried contrary to the bricklayer's wishes, they could readily be mistreated in service and thereby eliminated. Succeeding this period is that of buying by the purchasing agent, but here, too, progress is retarded in another manner.

The purchasing agent's objective is to buy refractories at the lowest possible price and the suitability of the brick bought is often a secondary consideration. Such a means of buying may or may not prove to be economical. If all refractory materials possessed the same properties to the same degree, such a system would be efficient and practicable.

Maximum life of the refractories under a given set of conditions in service will be obtained only by employing brick that have the specific properties essential for that service. It is logical, therefore, to consider the properties of the brick that are to be purchased. This resolves itself into the use of specifications. Experiences with specifications to date, however, have not always been satisfactory and a little thought will reveal the cause of this condition.

A practical and valuable specification must set forth requirements for the brick that will allow it to render the maximum practical life in the position in which it is to be used. In order to make it practical, however, the requirements must be such that materials can be manufactured so as to meet them at a price satisfactory to both parties. There are definite limitations to the development and combinations of properties that can be made in any refractory product. As a result of these conditions, most specifications now in use are of more or less questionable value. As progress is made in the study of service conditions and as more adequate test methods are developed, it will be possible to formulate specifications that will be highly satisfactory. Aside from their value to the consumer, they will stimulate the development of special refractories to fulfill the requirements set forth. It is unreasonable to expect the manufacturer to extend his interest in research or the development of his product beyond a certain degree, without an appreciation of or demand for such improvements.

At the present time it is possible to formulate specifications for most furnace operations that will be of considerable value in spite of their shortcomings. They will offer a means of eliminating in a definite way the types of brick that are unsuitable for service and leave a group that offer the best possibilities. Since it is not possible with our limited knowledge to actually obtain by specifications the best brick on the market for a given service, the next best means is that of using a brand from the eligible group by the present day specifications just mentioned.

In order to formulate a specification of merit, it is essential that the most experienced technicians of the consuming and producing interests cooperate to supply the information that is vital for its success.

In connection with specification, there should be mentioned the influence that they exert on the trade in general. It will mean that the same language concerning service conditions and operations, properties of refractories and test methods will be used by all. They will set down a definite scientific outline of the refractories problem in each type of service and will supply a clearly lefined objective for the manufacturer to follow. The development of the refractories field on such a scientific and organized basis should mark one of the greatest periods in its history of progress.

Another means of increasing the utility of refractories is in the method of their use. Frequently the furnace design and its operation are decided upon without due consideration of the limitations and properties of the available refractories. In the recent meeting of the Fuels Division of the Society, the writer presented a paper [1] showing the relation between conditions of service and properties of refractories. Great advancement can be accomplished in this direction by the consumer assisted by the producer. The correcting of such conditions undoubtedly offers a greater field for progress than does the development of novel refractory materials.

In considering the development of the refractories themselves, the question of demand is basic. As mentioned, the enumeration of specific logical requirements by the consumer will largely influence the rate of progress. At present it is difficult to determine and weigh the importance of certain properties of brick to be used in the various types of service. There is also the question of the sale price of the brick when developed. Considerable difference in opinion exists as to the price that can be paid for brick that will increase the average service period. Will it be of interest financially to the producer to develop such superior products?

Steady progress is being made in all branches of production in the selection of raw materials, methods of forming and in firing. The replacement by machinery of the human element is an important factor in producing more uniform brick. In the firing process the uniformity is being assisted through the application of data obtained in careful studies of kiln firing. The adoption of tunnel kilns is also a noteworthy factor.

The following comments regarding the various classes of refractory possibilities for advancement are given, some of which may not prove practical upon application.

Clay Refractories

Clay refractories are usually made of a mixture of flint and plastic clays. A wide range of properties can usually be obtained by blending various percentages of these clays. In addition to such mixtures various methods of manufacturing are employed to produce desirable characteristics in the brick.

The immediate outlook for greatly improved clays does not appear promising. Mention should be made, however, of the opportunity of purifying clay for use in manufacturing blast furnace brick. The iron compounds present in nearly all refractory clays are causes of the disintegration occurring in these linings. Clays are treated for use in manufacturing glass-house refractories and many of the other ceramic industries employ processes for purification, such as weathering, washing, elutriation and magnetic separation.

The chemical composition of the various clays used in the brick must be of importance to their behavior in service. For instance, if clays are employed in a brick mixture that vary widely in the silica-alumina ratio and total percentage of fluxes, there will be, in the heat treatment of service, various chemical reactions occurring in these dissimilar constituents. A refractory cannot be expected to maintain its original properties in service while such conditions exist within the brick. Obviously dissimilar physical properties of the ingredients will have like effects. Such reasoning applies to all types of refractories and is not limited to clay refractories.

Another field of possible improvement is that of the control of the percentage of the various particle sizes of the materials used in compounding the batch. A study of this subject is now in progress [2] and preliminary data appear to be of value. It is well known by practical brick men that the structure of the brick is often more important than the chemical composition or refractoriness. The structure of the finished refractory is not only dependent upon the process of manufacturing, but also upon the physical and chemical characteristics of the materials employed in compounding. Therefore, careful studies of the effect of calcined flint or plastic clay upon the brick should be conducted.

There are many fields for investigation along such lines that will probably result in greater progress in the production of more useful refractories than will the employment of new raw materials.

Silica Brick

The noteworthy innovation of recent years in the manufacture of silica brick is the adoption of the silica brick machine. Such mechanical molding of the brick should be an important factor in the production of more uniform brick. Evidently the properties of such brick are equal to the hand-made product and should be superior for obvious reasons.

Another aid to the production of a highly uniform product would be the use of continuous kilns. This method of firing is now being seriously considered and will undoubtedly be employed in the near future.

A fruitful field for development of more useful silica refractories should be that of producing a dense silica brick. Such a brick would be a better heat conductor for muffles, coke oven walls, regenerators and such types of service, as well as being more resistant to most types of slag action.

Diaspore Refractories

The high alumina content of the diaspore refractories make them resistant to unusually high temperatures. This fact, along with their chemical nature make them of particular value for a number of service conditions. Their utility can be extended, however, by minimizing their probable shrinkage in service and by increasing their density. A means of affecting these properties is now being studied and to date the results are promising.

The Mullite Group of Refractories

The possibilities resulting from the use of the Sillimanite group of minerals (cyanite, andalusite, and sillimanite) for refractories has been a live subject in recent years. The physical and chemical properties of these materials are of a most promising nature. There proper use in brick making has, however, required careful study and the full merit of the present products has not be established in many types of service. They appear to be of particular value in glass-making furnaces. Their field will broaden in the future; filling the positions that cannot be satisfactorily met by other materials. The comparative cost of the raw materials will necessarily limit their use and place them in the class of specialties.

A noteworthy refractory material of this class is the cast mullite. This product, which is simply a casting of an electric furnace melt, is of considerable interest. Raw materials of the composition necessary to produce mullite are used for the melt and, after being cast, the shapes are annealed. The finished product has almost no pore spaces and is therefore, of special interest in slag action. It has been found that the addition of low percentages of certain materials will substantially alter the properties of the finished casting, especially with regard to slag action. It is logical to expect that this principle will be applied to the manufacture of refractories of other compositions. Chrome, magnesite and spinel compositions should prove to be of value to the steel industry.

Chrome Refractories

In recent years chrome refractories have found wider use by reason of their improved properties. In order to manufacture such superior chrome brick, it is essential that the highest grade of chromite be employed. By reason of the quality of ore needed and the large tonnage consumed annually, the question of supply is important. Means of purifying or utilizing lower grades of ore should be studied. Chemical treatments or electric furnace refining are possibilities. The resistance of chromite to high iron slags makes it of interest for boiler settings in which a coal giving a high iron ash is fired. Their comparative weakness at these furnace temperatures and sensitivity to thermal shock precludes their use in this service at the present time, but future developments should extend their use to this service.

Other Refractories

In recent years highly calcined kaolin refractory has been marketed and like other special materials it is becoming established in certain limited uses. This product, by reason of the purity of the clay used in manufacturing and the exceedingly high temperature to which it is fired, possesses some unusual properties for clay refractories.

Mention should be made of the studies and the progress being made in the subject of testing refractories. Without adequate means of testing, progress in development and application of refractories is handicapped. Tests are the basis of specifications. The studies and experiences obtained in recent years have enabled technicians to develop noteworthy improvements in test methods and their use. Developments are leading to the simulation of actual service conditions and the lengthening of the time period of testing.

There never has been such interest in the field of refractories as in shown at the present time. Technicians of all classes are considering refractory problems from various angles. With constant study and cooperation between user and producer the whole field of refractories should make increasingly rapid progress in the future.

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