CHANGES IN RAW MATERIALS–HISTORY REPEATS ITSELF

Ruth Engel, Refractories Consultant, 121 Olde Farm Rd., Oxford, OH 45056
ruthengel@refractoryexpert.com

Ruth Engel

INTRODUCTION

Availability and cost of raw materials have always been a major driving force in the changes that have taken place in the manufacture of routinely used refractories. Concurrently, the users of refractories keep implementing process changes leading to ever more demanding environments, which can only be satisfied by continuously improving refractory properties. These issues, together with environmental concerns, have pushed refractory development and reliability into new realms and stressed the raw material side to produce new, cheaper and easily available materials that can be used to fulfill all of these requirements.

Alumina silica refractories have changed over time because of all of the above. In this article, I will be concentrating on the effect that raw material changes had on physical properties. In particular, I will follow the changes that occurred in fired alumina silica brick. Although the data and events presented took place many years ago they are applicable to today's conditions as the difficult raw material's market forces the manufacturer to continuously reformulate their product in order to maintain expected properties and utilize what is available at a reasonable price. It also highlights the user's problem of determining when a change has taken place, which could affect the life of the installation.

BACKGROUND

Professor Brosnan stated that "With the advent of phase equilibrium diagrams after about 1920, the modern era of alumina-silica brick began. At that point, scientific principles guided the development of fireclay brick rather than trial and error" [1]. The manufacturing progression went from fireclay to ever-higher alumina bearing brick. Alumina silica refractory brick consumption peaked in the late 1970s to early 80s. Their use has decreased since as the result of many variables: advances in castable technology, development of alumina-magnesia-silica brick, processes requiring other refractory chemistries, etc.

In the United States, the cheap availability of high purity fireclays was reflected in brick properties, which were comparable to higher alumina refractories, made in other parts of the world. In particular, super duty brick (45% Al_2O_3), was once the standard product used in many applications. Little thought was given to either the provenance of the clay or the expected physical properties of the brick as many companies manufactured similar products. With the advent of steel ladle metallurgy, which led to longer contact times and increasing metal temperature, the use of fireclay brick was discontinued and more refractory types of alumina brick, 50% then 70% and now 85% with or without magnesia additions using high purity bauxites and fused aluminas, have taken their place.

Table 1 shows the continuously higher refractoriness of the brick as a function of their increasing alumina content [2]. Another consequence of the increase in refractoriness is that the PCE (Pyrometric Cone Equivalent) test is no longer carried out and the lower temperature Hot Modulus of Rupture or Hot Load are no longer important because the expected use temperature is considerably higher. Table 1 also shows how high temperature strength increases with the higher alumina levels and this was one of the reasons for greatly improved steel ladle life [2].

RAW MATERIAL CHANGES

In the late 1980s and early 1990s a major change to the alumina silica raw material provenance took place because the easily mined US deposits were exhausted, Guyana's mine was flooded and newly developed Chinese bauxite mines provided cheap and plentiful material. Consequently, they started to be used. Prior to this time, most bauxite came from Guyana which produced very high purity bauxite and many high quality deposits could be found in the southeast United States. These latter deposits were generally known as the source of SEUS grain.

Table 2 shows the chemistry and physical properties of several 70% alumina brick [2-4]. When available, the year the testing is included. Note that although this table was originally published as reflecting properties of 70% Al_2O_3 brick, today, the Early Chinese Bauxite-1988, would not be considered part of this group. The impetus for this work was an unexpected high wear rate of brick in steel ladle applications, leading to an unexplained dramatic decrease in life.

Of the commonly reported properties: the brick chemistry is quite consistent, with some variability shown in the TiO_2 level, the bulk density similar between products, but the apparent porosity shows some variation. The differences between the products become apparent when looking at the high temperature test results. The steel ladle problem was eventually traced back to a decrease in hot properties as shown by the lower hot modulus of rupture (ASTM C583) and poorer hot load (ASTM C16) values. This change could be summarized by "the outstanding product of the late 1970s has shown a distinct drop in properties at high temperature... Raw material substitutions have diminished the high temperature proprties…" [3]. As these were fired brick, the number of standard ests available for determining properties is extensive. In addition, it the time of this problem many producers of refractories, as well is their users, had substantial laboratories where testing could be carried out easily and quickly. As a result, the problem could be addressed in a timely fashion. For comparison, data for a current-y produced brick was added. Note its physical properties are in he same range as those produced using the Guyanese bauxite and hat minimal hot properties are provided.

DISCUSSION

Today this problem has only historical significance because, after undergoing a learning curve, the refractory manufacturers were able to produce brick with good high temperature properties using Chinese bauxites.

What we can take away from this experience is that room temperature tests may not adequately differentiate between same category products. This can lead to problems when the user is not aware of the possible ramifications a new raw material could have on the product and consequently expect properties, in actuality service life, which are not met.

Many new types of refractories have been developed since these studies were undertaken: considerable brick quantity is no longer fired but resin bonded, many alumina brick are made out of fused product and many refractories are of basic composition. These choices have not decreased the difficulty in securing a steady and reliable supply of raw materials at a reasonable cost. In today's economy, this is again a major challenge to the producer's ability to deliver a consistent product. Their refractory knowledge and ingenuity has allowed for the continuing production of reliable materials, even though at times changes have to be made to accommodate the market. It is important that these changes be communicated to the user in such a way that the possible implications are understood.

Each refractory application requires a unique set of properties for it to be successful. Selecting refractories which optimize these values while minimizing their cost will lead to a best overall practice. To achieve this, knowledge of as many pertinent parameters as possible and close cooperation between all parties is needed.

If you have comments about this column or suggestions for future topics please visit me at www.refractoryexpert.com and I will try to address them.

REFERENCES

1. Refractories Handbook, Charles Schacht ed., p. 81, 2004.
2. R. Engel, R. Marr, E. Pretorius, "Refractory/Slag Systems for Ladles and Secondary Refining Processes", Keeping Current Series, I&SM, 1996.
3. B. Baker, R. Shultz, "The Importance of High Temperature Properties in Refractory Material Selection", Fall Meeting of the Refractories Division of the Am. Cer. Soc., Oct. 1989.
4. Internet: 70% alumina brick, data sheet, 2010.

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Table 1. Comparison of Chemistry and Properties of Steel Ladle Brick

	Bloating Ladle Brick	50% Al_2O_3 Volume Stable Brick	70% Al_2O_3 Volume Stable Brick
SiO_2	67.2	45.4	25.2
Al_2O_3	26.1	49.5	70.6
TiO_2	1.3	2.2	2.9
Fe_2O_3	2.0	1.5	1.0
CaO	0.2	0.2	0.05
MgO	0.4	0.4	0.1
K_2O+Na_2O	2.7	0.7	0.1
PCE	20-33	>34	37-38
Bulk Density (g/m^3)	2.28	2.44	2.53
Apparent Porosity (%)	13.0	13.0	17.0
Cold Crushing Strength (kPa)	53,500	52,800	45,800
Hot MoR (kPa)			
@ 955°C (1750°F)	3,000	15,100	12,000
@ 1095°C (2000°F)	3,500	19,300	12,200
@ 1260°C (2300°F)	1,500	16,700	8,400
@ 1480°C (2700°F)	0	140	2,600
Linear Expansion (%)			
@ 540°C (1000°F)	0.35	0.26	0.24
@ 1095°C (2000°F)	0.35	0.58	0.60
@ 1315°C (2400°F)	3.85	0.73	0.76
@ 1450°C (2640°F)	NA	NA	NA
Permanent Linear Change (%)			
Schedule E (1290°C)	+10 to +16	-	-
Schedule C (1600°C)	NA	+1.3	-0.4 to +1.0

Table 2. Comparison of Chemistry and Properties of Fired 70% Alumina Brick

Raw Materials	Guyana Bauxite -1977	Early Chinese Bauxite-1988	50% Chinese 50% SEUS	All Chinese Bauxite-1994	All SEUS Grain	Chinese Bauxite-2010
Al_2O_3	71.8	76.3	69.6	72.0	68.2	69.9
SiO_2	22.9	16.8	22.4	23.0	27.0	24.1
TiO_2	2.9	3.6	2.9	2.9	2.9	3.2
Fe_2O_3	1.5	1.3	1.7	1.4	1.6	1.5
CaO	0.2	0.1	0.1	0.2	0.1	0.2
MgO	0.2	0.2	0.4	0.2	0.2	0.2
K_2O+Na_2O	0.5	0.8	0.6	0.4	0.2	0.9
P_2O_5			2.8			
Total % auxiliary oxides	5.3	6.0	5.7	5.1	5.0	6.0
Bulk Density (g/cm^3)	2.57	2.63	2.66	2.63	2.57	2.59
Apparent Porosity (%)	20.2	21.1	17.1	19.0	14.5-18.0	18.5
Hot MoR (kPa)						
@ 1260°C (2300°F)	7000	6850	5109	4800	9584	
@ 1480°C (2700°F)	2100	1700	3048	1620	3054	
Hot Load (%)						
@ 1450°C (2640°F)	-1.5	-0.4	-0.7	-	-1.1	
@ 1510°C (2750°F)	-	-	-	-3.1	-	
@ 1650°C (3000°F)	-11.0	-22.0	-17.6	-	-7.7	
Permanent Linear Change (%)						
@ 1600°C (2910°F)	+4.0	+6.0	+4.6	+2.4	+2.0	+4.1

Editorial from the Assistant...

by Todd Sander, *RAN* Assitant Editor

I'd like this opportunity to publically and personally thank Mary Lee, *RAN* Assistant Editor Retired, for her years of service to the publication. I have learned recently first hand the job she made seem effortless from the perspective of the observer is not what it appeared to be. Although, as with all professions, it is characteristic to the title that the observer thinks to themselves that they too can do what they do.

We all may have seen a home improvement show and been inflated with confidence and ignorance and the desire to accomplish the same in our own home. It is only later that we discover what appeared simple in the hands and care of a pro evolves into a litany of never-ending trips to the home center and countless additional hours of unanticipated toil, labor, and expense. Although the amateur may yield a functional product and take pride in its birth at his hand, it is usually lacking the fit and finish a true professional imparts. It is with this perspective I hope you judge our product, *RAN*, in this period of transition.

As our senior editor iterated, I further implore that you, the reader, consider contributing to the publication in any way you may feel compelled. Although advertising and donations are what makes this publication both possible and free to the reader; it is its content that we hope the readership both enjoys and can appreciate from. In that regard, I urge readers to seriously consider submitting copy to *RAN* for publication. You may think you might not have anything appropriate to submit; however, copy can be of any type and can range widely.

Examples of copy include but are not limited to:

- Comprehensive research submitted to *RAT* (Refractory Applications *Transactions*) for peer review
- Other research, observations, or experiences; failures to prove hypthesis are often the most valuable yet unpublished works and requires the most courage of author to forward. Success and improvement is easy to report.
- Student research from a simple summary/abstract to something more extended. (A great way for students in the industry to forward their name and work prior to seeking employment!)
- A retiree's retrospective on their careers and the industry, how it was then and is now, how they see the future.
- An opinion piece on anything related to our industry, as short as a paragraph or as long as you require to opine.
- Open letters to raw material suppliers, refractory producers, refractory users, regulatory officials, academia, etc.
- Reader mail, "I enjoyed the article...in particular...but...however...in our experience...well done...its 2 not 3...etc." We don't have to use your real or full name if you desire.

I formally challenge each of our **corresponding editors** acknowledged on page 2 to contribute at least one article a year of any type to *RAN*; I will not exclude myself from the contest.

As an engineer, I would be happy to assist and work with anyone on their submission from editing, to preparation of tables or charts, to rendering figures and diagrams. I look forward to working both with and for you in the coming issues.

I can be reached at rannews@mst.edu or 573.341.6561