

Invited paper presented at AISE Conference, Chicago, Sept. 10-13, 2000.

**An Overview of DOE's Program to Recycle/Reuse Spent Refractories
as a Slag Conditioner and to Extend Refractory Service Life in the EAF**

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ABSTRACT

Refractories removed from EAF service are typically landfilled. Interest in recycling/reusing the material is growing. A joint program between the USDOE and Steel Manufacturers Association is evaluating spent refractory recycling/reuse, with emphasis on in-house applications as a slag conditioner and as a refractory raw material. The joint program is also evaluating refractory wear modeling and service life extension. A review of progress on controlling EAF slag chemistry and properties with additions of basic spent refractories, on refractory wear modeling, and on how these goals relate to service life extension will be discussed. Computer models have been developed to predict dual saturated slag chemistry for foaming, to model and control the slag foaming process, and to predict refractory wear when "what if" system changes are made. Evaluation and refinement of these programs are being made in steelmaking environments.

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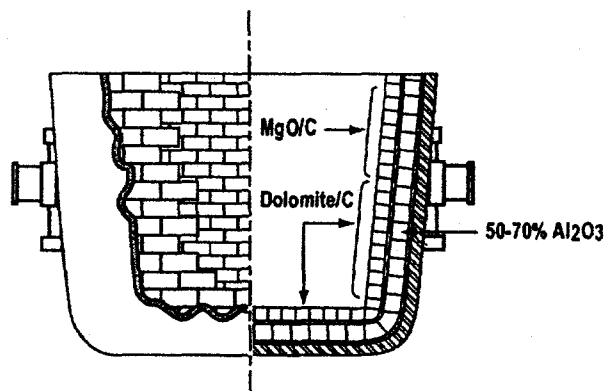
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INTRODUCTION

Refractory materials removed from service in the steel industry have typically been landfilled. The reuse or recycling of these materials after removal from service in the United States has been principally limited to the textile and fiberglass industries. Where recycling is practiced, it has been driven by economics, legislation, or by corporate efforts to reduce or eliminate industrial waste. Complex issues have limited recycling efforts. These include contamination, the amount and frequency of refractory wastes generated, difficulty in segregating material, shipping costs, beneficiation costs, performance issues in materials where refractories are reused, and the low cost of raw materials. Refractory reuse/recycling efforts in the Canadian steel industry have been driven by legislation to reduce industrial wastes that are landfilled, forces that do not exist in the United States, where most refractory material is landfilled.

Spent refractory material from the steel industry typically include alumina-silicate, carbon, or basic materials (magnesia, dolomite). Usage of some refractories, such as prefired shapes or those containing chrome oxide, is on the decline, while the use of monolithics or materials like alumina-magnesia-carbon (AMC) refractories is increasing. Refractories can have a sintered, carbon, or chemical bond (primarily cement) with/without carbon additions, metallic antioxidants, or other additives. The same class of refractory materials may vary widely between different refractory manufacturers, each using his own proprietary way of manufacturing the material. The refractory material may be altered slightly (customized) by a producer for different users in his effort to optimize material performance. Steel producers have additional complications in recycling spent refractory materials. These are caused by the difficulty in segregating and storing zoned material (zoning is the use of different types of refractory material in different locations to optimize material performance). Zoning and the removal of spent refractory material from a ladle application is shown in figure 1.



(a.)



(b.)

Figure 1 - Refractories in a steelmaking ladle (a) zoned refractories for improved service and (b) being removed after service.

When refractories are evaluated for recycling, the amount of material removed from an application is typically less than originally applied because of wear and degradation that occur during service. The amount of refractory material eligible for recycling can be reduced further because of contamination that occurs during use, removal, or storage. Contamination from use (1) can be caused by the process (slag or metal infiltration), from material changes that occur during use (anti-oxidants forming oxides, nitrides, or

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carbides), or from changes brought about by the process (chrome +3 going to the carcinogenic +6). All complicate recycling. Growing concerns over legislation, the environment, landfill space, and future liability have acted as driving forces for corporations to consider recycling (2). Other factors such as product stewardship, ISO 14000 certification programs (environmental management systems), pressure from refractory users, company policy, the high value of some refractory components, perceived marketing advantages, or landfill costs have also acted to encourage recycling. The effects of some of these forces is visible in Canada, where laws to reduce industrial sent to landfill encouraged the start of refractory recycling efforts at steel companies like Stelco-Hilton Works and Dofasco-Hamilton. The options for reuse of spent refractory materials is greater in an integrated shop versus a mini-mill (EAF shop). Without a specific driving force, recycling of refractory materials must be customized for each company. Possible applications for spent refractory materials are listed in table 1. Many of these have been practiced industrially or have been shown through research as possible applications for spent refractory material.

Table 1. Possible applications for spent refractory materials

Refractory component	Roofing granules
Slag conditioner	Tile body component
Component in cement, aggregate for concrete	Raw material for glass
Ferro alloy (high chrome containing materials)	Building component
Fuel source (SiC, C containing materials)	Insulating powder
Carbon, silicon source	Filler for bulk items
Grog in ceramic materials	Landscape material
Waste neutralization/treatment (acids, pathogens)	Soil stabilization
Highway road aggregate/subbase	Soil conditioner
Abrasive	

Before a refractory user initiates a recycling effort, they should first consider what reductions in refractory waste generation can be brought about by changes in the manufacturing process or by using refractory materials with longer service life. It should also evaluate changes that can be made in the refractory material to make it more recyclable or to use a refractory that is recyclable versus one that is difficult to recycle. The refractory user should also consider internal uses for the refractory wastes. Economics related to the changes must be considered in each situation.

Technological advances have played a role in improving refractory service life, thus reducing the amount and frequency of spent refractory materials removed from an application. Examples of the impact of technology are in steel furnace design, where open hearth furnaces have been displaced by BOF's and EAF's. Other changes increasing refractory service life are improved plant design and operation, ladle metallurgy adjustments, improved maintenance and repair schedules, better slag and metallurgy control, and slag splashing (3). Improved refractory materials; better customer service by refractory producers; hot patching; monolithic materials; zoning; gunning; subcontracted refractory installation, tearout, and maintenance; the practice of the endless lining concept (4); and refractory wear sensing have also acted to improve refractory life and reduce the amount of refractory wastes generated in steelmaking. Future furnace designs to reduce refractory wastes may include the used of contour lining to put a refractory lining in its equilibrium state from the initial use.

The Albany Research Center and Argonne National Laboratory are working with a number of EAF steel companies to reduce or eliminate refractory wastes. This research is being conducted under a joint program between the Steel Manufacturers Association (SMA) and the Office of Industrial Technologies, USDOE.

The joint program has two broad goals: 1.) improving the service life of refractory materials used in the slagline areas of EAF's and 2.) recycling the spent refractory materials. Twenty-one SMA members are participating in this program. In addition to the SMA members; Chaparral Steel, Georgetown Steel, Bayou Steel, SMI Steel-Birmingham, Martin Marietta Magnesia Specialities, and Baker Refractories are collaborators in the program. The first program goal, improving the service life of refractory materials used in the slagline area of EAF's, is directed at reducing the amount of refractory wastes generated by EAF steelmakers. This will be accomplished by modeling and controlling slag foaming, by modeling refractory wear to predict wear when "what if" system changes are made, and by developing wear-resistant repair materials from spent refractories. The second goal, to recycle spent refractory materials removed from EAF service, is directed at finding applications for spent refractory materials. Refractory recycling/reuse is directed at in-house applications because they are thought to have the greatest chance for implementation. Research on three portions of this program, 1.) slag foaming and control, 2.) predicting refractory wear, and 3.) recycling spent refractory materials, will be discussed below:

Slag Foaming and Control to Reduce Refractory Wear

Basic refractories can be reused in EAF's as a slag conditioner. When reused as a slag conditioner, spent MgO/C or dolomite refractory material help to saturate the slag with MgO, satisfying phase equilibrium requirements of the slag. This reuse reduces wear on the working lining that had previously acted as a source of the MgO.

Pretorius (5) discussed the important connection of MgO saturated slags to slag foaming and refractory wear. The source of MgO in the slag can be dolo-lime additions to the slag, waste MgO/C and dolomitic refractories added to the slag, or the working face lining refractory lining (dissolving into the slag). Part of the goal of the joint OIT/SMA program is to reuse basic refractories as a slag conditioner in the initial EAF charge. Pretorius's model shows slags that are under-saturated with MgO may be too thin (runny) for proper bubble retention during slag foaming. This condition in an EAF would cause high refractory wear as the slag "equilibrium" level of MgO would originate from the hot face refractories. If the slag is over-saturated with MgO, it may be too thick (dry or crusty) for proper bubble retention. The ideal slag is near MgO saturation (creamy appearance), and has good bubble retention.

In trial tests at Nucor-Darlington, Pretorius targeted a slag chemistry near ideal MgO saturation (5). As a consequence of controlling the slag chemistry in this area, Nucor found reduced refractory wear and creamy, good foaming slags. In addition, an energy savings of about 5 pct per ton of steel produced was largely attributed to the slag control versus other system changes that were made. A survey of EAF operators in the USA indicated that most do not have a good knowledge or control of slag foaming. Because of the lack of slag chemistry control and because of the impact this control has on refractory wear, a computer program was written at Albany to predict correct slag chemistry based on raw material furnace feed and past experiences. The program predicts slag chemistry and indicates a target MgO saturation level as shown in figure 2. The goal of the program is to reduce refractory wear, extend the service life of hot face refractory materials, and reuse spent refractory materials. The program was written with the assistance of JE Baker Refractories Co.

Existing phase diagram information was used to construct the slag chemistry model for the OIT/SMA program. It is able to predict dual saturation chemistry (MgO and/or CaO) in an EAF steelmaking slag using a targeted slag chemistry. The targeted chemistry is for ideal slag foaming and minimizes MgO/C brick wear due to slag corrosion. This is represented by slag chemistry path 2 in figure 2 and is a creamy slag. Path 1 represents an over-saturated slag that is thick and crusty and 3 represents an under-saturated slag that is thin and runny. The model incorporates five major components of a slag (SiO_2 , CaO, MgO, FeO,

and Al_2O_3), temperature (1500°-1700°C), the $CaO/(SiO_2+Al_2O_3)$ ratio, and the $Al_2O_3/(SiO_2+Al_2O_3)$ ratio. Efforts at the Albany Research Center are currently directed at measuring several synthetic slag viscosities from a number of EAF slag compositions to validate the slag chemistry model. Actual slag compositions from a steel plant participating in the research were compared to the model's predictions and are listed in table 2. The data indicated that these commercial slags were very close to ideal.

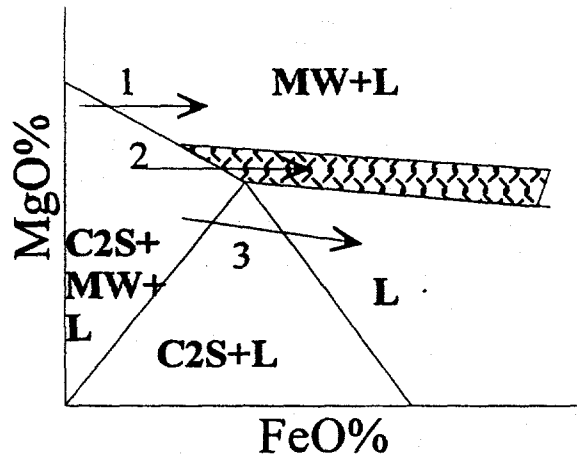


Figure 2 - Targeted Slag Chemistry in the Slag Modeling and Control Program for a MgO Saturated Slag

Table 2 - Actual and Predicted Slag Compositions From an EAF Furnace Shop Participating in the OIT/SMA Program

Slag Sample	Al_2O_3	SiO_2	CaO	$FeO+Fe_2O_3+MnO$	MgO
# 1 - Slag	5.70	14.07	37.10	33.91	9.22
- Model	5.86	14.52	37.45	33.91	8.23
# 2 - Slag	5.47	14.31	36.00	34.96	9.26
- Model	5.61	14.72	36.24	34.96	8.47

The slag chemistry information will be incorporated into a larger program used to model and control slag foaming in the EAF. This program is being written at the University of Alabama. This larger slag modeling and control program is currently undergoing testing and refinement at a steel producer. The ability of the program to predict relative slag foam height is shown in figure 3. The program learns from previous operational data and uses the information to predict slag foam height based on EAF data currently being monitored. Future plans are to evaluate the program using different furnaces and to incorporate the saturated slag chemistry program. After additional testing and refinement of the larger model, it will be evaluated under actual service conditions and made more robust. The extended slag modeling and control program will allow spent refractory materials to be added as EAF slag conditioners by calculating the overall slag chemistry. If successful, refractory wear during a heat should be reduced. The program's evaluation and refinement should occur over the next year.

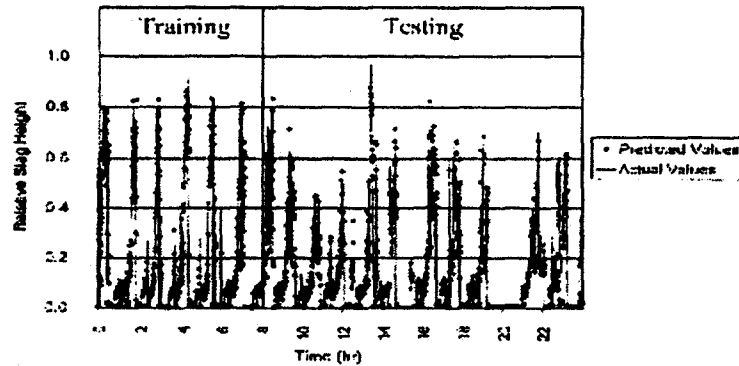


Figure 3 - Slag Foam Height Predictions Based on Furnace Input Data

The consequences of spent refractory additions to EAF's slag are being investigated as a part of the joint project. A few EAF shops have added spent basic refractory materials as part of the slag conditioning charge in the EAF with no adverse effects to EAF furnace operations noted. The spent refractory wastes are crushed and added with the dolomite/lime or lime charges to the furnace. This type of spent refractory reuse has been practiced inconsistently by industry and is poorly documented. A concern of adding spent refractory materials to the EAF slag is whether the MgO material balance needed for a saturated, good foaming slag will be kept in the correct range. There are also questions about if all of the spent refractory material will dissolve into the slag. The Albany Research Center is currently working with an EAF shop to evaluate the effects of adding crushed MgO/C refractory and crushed dolomite/C refractory to the initial slag conditioning charge. The spent basic refractory material additions will be crushed below one inch in particle size and added to the initial slag charge (in addition to the dolomite/lime materials currently added). Dust collector fines from the EAF will be evaluated to see if significant quantities of the spent refractory material become included in these fines versus becoming part of the slag. The EAF slag will be evaluated to determine if spent refractory material dissolves in the slag.

Predicting Refractory Wear

The wear of MgO/C refractory materials used to line an EAF are being evaluated by Argonne National Laboratory. Synthetic slags with low MgO, high FeO, and low calcia/silica plus alumina ratios are being used to accelerate refractory wear because of the low corrosion that occurs in samples using EAF slags. Test temperatures ranging from 1550°-1660°C are being used to simulate real furnace conditions. Initial results are for MgO/C with three different carbon levels (8, 15, 20 pct C), with fused and sintered MgO grain, and with/without antioxidants are being evaluated. Test samples made from refractory repair material with 30 wt pct coarse size fractions are also being evaluated as repair materials. The corrosion resistance of MgO/C refractory materials with 92 pct C at different temperatures is shown in figure 4. As expected, with an increase in temperature, the corrosion the test sample increases. A plot of the amount of material removed by slag corrosion as measured by the cross sectional area removed from a sample is plotted in figure 5 for a 15 pct C containing MgO/C sample made from large crystal sintered MgO grain. Again, as the temperature increased, the amount of material removed from a sample increased. Data of this type is being used as input in a computer model being developed by Clemson University. This model has the goal of predicting refractory wear without actually making furnace changes. The model is based on inputting desired "what if" system changes. Data is currently being measured to supply as input for the computer model.

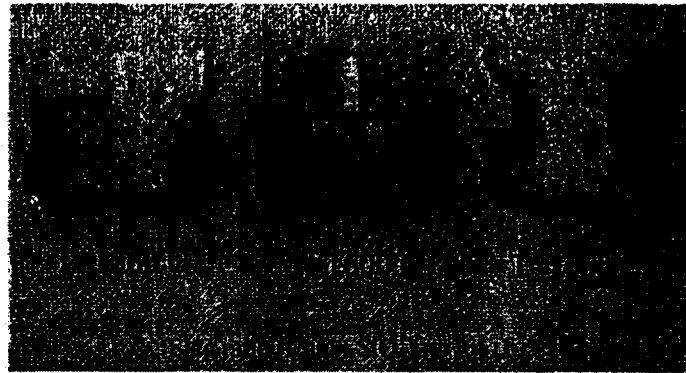


Figure 4 - Effect of Temperature on Slag Corrosion and Penetration on a Commercial MgO/C Refractory with 8 pct Carbon.

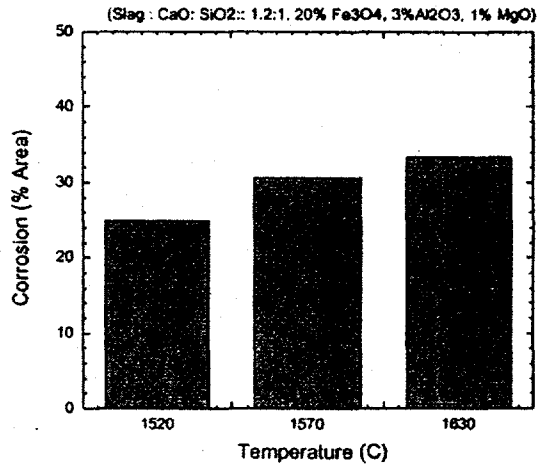


Figure 5 - Effect of Temperature on the Corrosion Resistance of a Commercial MgO/C Refractory Made From Sintered MgO and 15 pct C

Recycling of Spent Refractory Materials

Another goal of the OIT/SMA steel program is the utilization of spent refractory materials. The decision was made to target reuse of the spent refractory materials as repair materials (rather than as primary liner materials) and as a slag conditioner (previously discussed). This is because of cost issues associated with beneficiation, the low price of virgin materials used in primary lining materials, and questions about spent material performance when compared to virgin materials. Gunned material used in the EAF for repair applications serve more as a sacrificial lining due to their high porosity (20-30 pct). With high lining porosity, slag infiltrates and easily attacks the refractory. Raw material purity is not as critical in these applications versus as a primary liner material. Martin Marietta Magnesia Specialities is working with the Albany Research Center and Argonne National Laboratory to evaluate the performance of spent refractory materials. Used refractory materials were obtained from 3 EAF shops and evaluated for consistency and chemistry. The spent refractory materials were removed from either the ladle or the EAF. Refractories

removed from the ladle were MgO/C, dolomite/C, alumina-magnesia-carbon (AMC), or alumina-silicate refractories. The alumina-silicate materials were a minority material, coming from the backup lining. Materials removed from the EAF were MgO/C refractories. The chemistry of these spent refractory materials were found to vary from lot to lot and from refractory user to refractory user.

The chemistry of used refractories will also vary with particle size, as shown in table 3 for dolomite/carbon refractories removed from a ladle. Note that about 6 percent of the material is recoverable as magnetic iron. Once the iron was removed from the refractory, about 68 pct of the sample was +3 inch or larger in particle size, about 13 pct was -3+1 inch, and 19 pct was -1 inch. Impurities were mesh size dependent and were generally elevated in the finer particle sizes.

Table 3 - Chemistry of Different Sieve Fractions for a Dolomite/C Lined Ladle

Oxide	Sieve Fraction			With Fe	Without Fe
	+3 in	- 3 + 1 in	- 1 in		
Al ₂ O ₃	4.59	3.68	7.05	4.66	4.91
CaO	52.3	53.0	46.6	48.4	51.0
MgO	40.3	32.8	24.0	34.1	35.9
MnO	0.01	0.45	1.28	0.29	0.31
Cr ₂ O ₃	---	0.02	0.06	0.01	0.01
TiO ₂	0.01	0.13	0.29	0.11	0.12
Fe	0.01	0.01	0.01	5.8	---
FeO	1.71	2.20	4.72	2.21	2.33
Fe ₂ O ₃	0.01	0.01	0.01	---	---
SiO ₂	1.17	8.34	9.90	3.57	3.76
C	2.15	0.76	0.87	1.62	1.71
S	0.01	0.06	0.07	0.02	0.02

When dolomite materials are being evaluated for reuse, the short life they have due to room temperature hydration must be considered. This hydration changes brick chemistry and particle sizing, limiting material reuse. MgO/C refractories also hydrate, but at a much slower rate. This slower hydration does not limit reuse applications. The hydration of dolomite and MgO/C refractories is shown in figure 6.

Metallic antioxidants added to many types of carbon containing refractories cause expansive behavior when they are removed from service and aged/weathered. During steelmaking use, the metallic antioxidants form oxides, carbides, or nitrides. These compounds react with water on removal from service to form hydroxides, ammonia, other gases. Tests were made to age the refractory and eliminate some of these disruptive reactions. Results indicated that after 6 months, all reactions with the environment were not completely eliminated. This was confirmed by observations and lab experience of Martin Marietta.

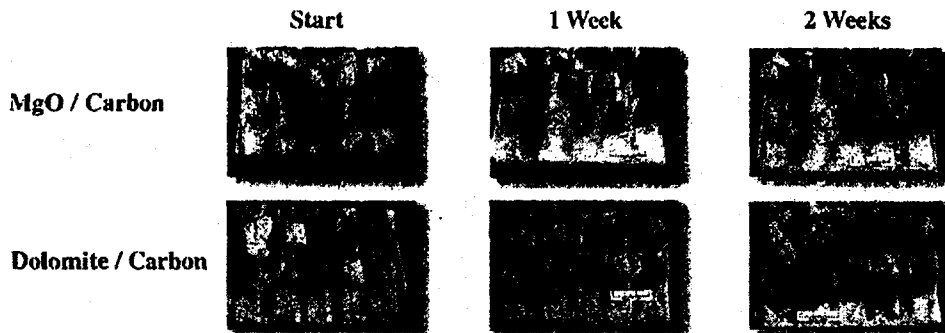


Figure 6 - Age Tests of Different Refractory Materials

Another recycling issue experienced in the program was the inability of a steel producer or mill service to segregate the refractory materials on removal from ladle applications. Refractory materials are frequently zoned for maximum performance when they are installed (previously shown in figure 1). During removal from service, refractory materials from one zone of a ladle can become mixed with those from other zones. Some of the reasons for this are the difficulty in telling where one zone begins and ends, the speed exercised in material removal, and because of the size of equipment used to remove refractories from an application. Differences also exist in the quality and types of refractory materials removed by different steel producers. Segregation for reuse as a slag conditioner is not as critical as those applications targeting reuse in refractories. No applications other than reuse as a refractory raw material or as a blast furnace slag additive are known for AMC materials because of the mixture of MgO and Al₂O₃ in the refractory.

Martin Marietta Magnesia Specialities has conducted research to evaluate MgO/C and AMC spent refractories as repair materials. Thirty wt pct additions of spent MgO/C materials were made to a silicate bonded alumina repair mix. The particle size of the spent refractory added to the mix was between 1.0 and 4.8 mm. Cold crushing strengths of the refractory composition when prefired at different test temperatures are listed in table 4. They showed only a slight strength difference when compared to the standard mix made using virgin materials. Martin Marietta concluded that silicate bonded MgO repair mixes containing MgO/C spent refractory could be used commercially.

Table 4 - Cold Crushing Strength Data for Repair Mixes Made Using Spent Refractory Materials

Treatment Temperature	Repair Material Room Temperature Crushing Strength (psi)*			
	Silicate-Bonded		Cement-Bonded Alumina	
(°F)	No Addition	30 wt% MgO/C Addition	No Addition	30 wt% AMC Addition
250	685	763	1480	1220
1800	765	642	1040	874
2400	660	504	1290	943
2910	960	870	7693	melted

*Crushing strength data were measured at room temperature on samples prefired to elevated temperatures

When 30 wt pct additions of spent AMC material were made to a cement bonded alumina repair mix, crushing strengths were lower for samples with the waste refractory material when compared to samples made from virgin raw materials (table 4). Excessive glass formation (melting) was indicated by 1600°C, where sample deformation occurred. This is due to impurities and to the mixture of Al₂O₃ and MgO in the sample. It is the opinion of Martin Marietta that the cement bonded alumina repair compositions could be reformulated to eliminate the formation of the glassy phase.

Slag tests are being preformed by Argonne National Lab on the MgO/C repair mixes formulated by Martin Marietta that used 30 wt pct spent refractory material. This information will help evaluate the suitability of MgO/C materials and will help provide input to predict material behavior.

CONCLUSIONS

Landfilling is the primary means used to dispose of spent refractory materials in the US steel industry. Environmental regulations and/or economic incentives have not played a significant role in the recycling/reuse of the spent refractory material. The Albany Research Center-USDOE and Argonne National Lab. are conducting joint research to extend refractory service life and to identify applications for the spent refractory material from electric arc furnaces. Computer models have been written that will identify correct slag chemistry for magnesia saturation in the slag and that will control the slag foaming process. Other models have been written to predict refractory wear when "what if" changes are made to the EAF. Applications for spent refractory materials are directed at in-house reuse as refractory repair materials and as slag conditioners. Models are currently undergoing refinement before being evaluated under actual service conditions.

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