Single-Step Ironmaking from Ore to Improve Energy Efficiency

(US Dept of Energy, 9/30/2003-9/29/2005)

Current blast furnace technology is a two-stage ironmaking process that requires that iron ore concentrate first be formed into pellets, fired at 1260°C, cooled, transported to the blast furnace, and then re-heated to approximately 1500°C to produce pig iron. This heating, cooling, and then re-heating wastes a great deal of energy, which would be saved if the ironmaking process had only a single heating step. Kobe Steel's ITmk3 process is intended as a replacement for blast furnace processing that produces "pig iron nuggets" directly from cold-pelletized iron ore concentrate in a single stage of heating. It is therefore more energy-efficient than the current technology. Iron nuggets are produced by combining iron ore concentrate with a reducing agent (finely ground low-sulfur coal), a binder, and a flux to form pellets. These pellets are then heated to approximately 1400 – 1500°C in a rotary-hearth furnace. Upon heating, the pellets self-reduce to molten iron and molten slag, which separate from each other to form a metallic pig iron nugget and a slag drop. Upon cooling, the slag separates cleanly from the metal nugget. The objective of this project was to determine how the transformation from powdered iron oxide to metal+slag occurs, to examine how the transformation is affected by temperature and processing time, and to determine the optimum conditions for producing iron nuggets as a function of temperature.

This project determined that, contrary to what had been believed by the developers of the ITmk3 process, the iron oxides did not directly react with the coal to produce pig iron in a single step. Instead, the transition consisted of the following stages:

1. Coal volatiles reacted with the iron oxides to produce "Direct Reduced Iron" (DRI)
2. Silicate gangue, coal ash, flux, and FeO melted to produce a slag, while the direct reduced iron began to melt due to dissolving excess carbon from the coal. This produced a mixed slag/metal product, "Transition Direct Reduced Iron" (TDRI)
3. The TDRI then fully separated into a liquid pig iron drop and a liquid slag drop. Upon cooling, this produced a pig iron nugget and a cleanly-separated slag nodule.

The time needed for this transformation was a strong function of temperature, with times ranging from over 40 minutes at 1400°C, to approximately 10 minutes at 1500°C. It was determined that industrial-scale rotary-hearth furnaces were producing nuggets with highly variable quality due to some pellets being heated more than others, with the cooler pellets having insufficient time to complete the transformation to iron nuggets. Uniform heating in the furnace is therefore key to maintaining satisfactory nugget quality.

Verification of Steelmaking Slag Iron Content, Recycle and Reuse of Steel Slags

(U. S. Dept. of Energy, 5/1/2001-4/30/2006)

A major market for steelmaking slags is for cement manufacture. However, many slags contain a significant amount of metallic iron, which can cause cracking and staining of concrete when the iron oxidizes. Removal of this iron from slag not only improves the suitability of the slag for cement manufacture, it also recovers metallic iron that has considerable value as metal and can then be recycled.

As a portion of the above project, slags from six different sources were processed by magnetic separation to determine the quantity of iron that could be recovered. All of the slags contained between 16% and 36% of magnetic iron that could be recovered readily by this means. It was also observed that the slags contained a certain amount of elemental carbon, which formed a hydrophobic layer. The carbon content was sufficiently low that it would not be a problem in cement production, but if a slag contained excessive amounts of carbon it would be straightforward to use a froth flotation process to remove it.

The cementitious properties of the slags were due to the availability of calcium-rich phases in the slags. The primary phases responsible that were identified by X-ray diffraction were Ca_2SiO_4, $Ca_{12}Al_{14}O_{33}$, and $CaFeSiO_4$. No free lime was detected in any of the slags, and the cementing phases that were seen in the diffraction patterns tended to be relatively calcium-poor compared to standard Portland cement. This suggests that these slags would be excellent additives for cement, provided that other sources of calcium were available and the carbon content was not excessive.

Prevention of Self-Heating of Swarf

(General Motors Corp, 4/19/1996-10/18/2000)

The investigators were approached by General Motors Corp. to provide assistance with a problem encountered in recycling the metal values from their machining waste, or “swarf”. Swarf consists of finely-divided steel particles with a very high surface area, and when exposed to air these particles undergo significant heating due to oxidation. In extreme cases, the swarf could heat sufficiently to catch fire, which made the material too hazardous to transport to recycling facilities.

A key problem of finding a solution to the self-heating problem was that this behavior could not be replicated in the laboratory, and so it was not possible to carry out laboratory tests to evaluate potential solutions. The investigators therefore first developed a sample collection protocol that preserved the self-heating properties of freshly generated swarf, and then designed a testing method that, for the first time, quantified the heat generated as the swarf oxidized. This testing method was then used to evaluate the effects of a wide variety of surfactant chemicals on the swarf oxidation, as well as the effects of moisture content.

It was determined in the laboratory that the primary effect of surfactants was that they would delay the onset of self-heating behavior, although they did not prevent self-heating altogether. However, this was valuable, as delaying the self-heating would give the opportunity to collect the swarf and isolate it from oxygen. It was also determined that there was a “window” of moisture contents where self-heating could occur. If the swarf was drier than the critical moisture content, there was insufficient water present to catalyze the oxidation and self-heating was much reduced. Alternatively, if the swarf was wetter than the critical moisture content, then oxygen was prevented from reaching the surface of the swarf particles, and again self-heating was reduced.

Based on these laboratory studies, in-plant studies were carried out where freshly-produced swarf was treated using the methods developed in the laboratory. These experiments were successful, and it was possible to develop a protocol that prevented the swarf from self-heating in the plant. This made it practical for the metallic swarf to be sold as metal scrap, so that the considerable metal values that they contained could be safely recovered.

Ultrasonic Removal of Mill Scale from Continuous Strip

(American Iron and Steel Institute, 11/1/2005-12/31/2005)

This work was carried out as an undergraduate student project, as the intent of the funding was to promote education of engineers to work in the iron and steel industry.

The removal of scale is important step in the galvanizing process. In order to obtain adherence of zinc to the steel, the oxide scale and lubricants must be eliminated. Steel pickling is the most common process of the removal of mill scale. It is often considered an environmental problem due to acid sludge. The elimination of the acids would reduce air and water emissions. The fundamental purpose of the research was to remove scale without the use of pickling. The alternative methods tested were ultrasonic, and electrolytic. Polishing with a wire brush, periodic reversal of the polarity of the electrolytic cell, mechanical treatments of the surface of the steel and thermal treatment were performed to improve ultrasonic and electrolytic processes.

Of the many trials performed, the most effective was a four step process consisting of bending, a thermal shock treatment, electrolytic treatment, and concluding with an ultrasound treatment. The amount removed was comparable to 3 minutes of acid with a mass removal per area of 8.16 g/m^2 and a standard deviation of +/- 0.953 g/m^2. Thermal shock treatment consisted of immersing the sample in liquid nitrogen, which was convenient for laboratory use but may not be suitable for industrial use. Other methods to cause thermal shock should be explored.

This process offers potential for the elimination of acid pickling. An opportunity for greater mass removal per area lies in the addition of new scale breaking techniques. If a stronger scale breaking technique could be developed, the scale would remove much easier. It should be noted that error could occur in the experimentation due to the temperature and age of the steel and scale. Our experiments were run on steel obtained from a hardware store. Removal results could be different while attempting to remove scale in process.

Chemistry and Physics of Taconite Agglomeration

(Minnesota Department of Natural Resources, 3/2/1999-6/30/2007)

While pelletization of iron ore concentrate has been used for many years, the process was for the most part developed empirically, and so the chemistry and physics of the actual pelletization process had not been studied. In particular, the behavior of binders was poorly understood, and it was not known whether bentonite clay binders were being used with the best possible efficiency, or whether lower-cost alternatives (such as local, non-bentonite clays or modified coal fly ashes) could be used as replacement binders.

A persistent problem in iron ore pelletization has been the difficulty in determining in advance how well bentonite from a given source would perform as a pellet binder. While many bentonite characterization methods have been proposed, none have proven to have a good correlation with binder performance. In this study, it was discovered that this problem was largely caused by very high levels of dissolved calcium compounds being retained in the moisture of iron ore concentrate filter cake. When bentonite came in contact with this moisture, the calcium ions degraded the bentonite performance dramatically, reducing the ability of the bentonite to absorb water by approximately a factor of four. Bentonites also varied in their sensitivity to calcium ions, and so some bentonites that performed poorly in distilled water, were actually the best choices for water containing large amounts of dissolved calcium.

In the course of examining the response of bentonite to dissolved calcium ions, a new standard technique for evaluating binder effectiveness was developed. This method used a highly standardized substrate (glass beads) to produce test specimens that were bonded together by the binder being evaluated. This method not only produced highly reproducible results, but also gave excellent correlation with binder performance when it was actually used to bind iron ore concentrate pellets.

Examination of glass beads bonded with bentonite under a scanning electron microscope showed that the binding mechanism of bentonite was different than had been believed previously. Instead of dispersing into a uniform suspension that coated the particles, the bentonite was found to be spread over the surface of the particles, drawing into sheets and fibers that bridged between the particles. Based on this observation, a new mixing method was developed, “compressive shear mixing”. Instead of mixing the particles conventionally, which tended to tear the particles apart from each other, the compressive shear method presses particles together so that they slide past one another. This takes advantage of the tendency of bentonite to form sheets and fibers, and reduces the amount of bentonite needed to produce a given bonding strength by 50%. This produces a marked savings in bentonite requirements. It was also determined that the compressive shear mixing could be used with other clays. Using this method, locally-produced clays that previously had been considered to have insufficient binding capability, had their performance enhanced to the point that they were competitive with conventionally-mixed bentonite.

Production of Inorganic Pellet Binders from Coal Fly Ash

(Southern Illinois University, 9/1/1994-8/31/1995, US Dept of Energy, 9/30/1997-9/29/1999)

When iron ore concentrate is pelletized to produce blast furnace feed, a key component of the pellets is the binder that holds them together until they can be fired to give them sufficient mechanical strength. The traditional binder used is bentonite clay, which is mixed with moist iron ore concentrate filter cake before pelletization. The bentonite bridges between the iron oxide particles in the pellet, so that when the pellets are dried they remain intact until they can be fired. The iron industry competes with other industries for high-grade bentonite, which has restricted bentonite availability and increased the cost, and so alternative binders would be valuable.

An alternative to bentonite binder, is binders based on coal fly ash. The chemical composition of fly ash is similar to that of bentonite, so their use will not disrupt the chemistry of the finished pellet. Fly-ash-based binders were found to give adequate pellet strength at dosages very similar to the dosages normally used for bentonite binders, although the binding mechanism was determined to be different. While bentonite binders produce a physical bond between iron ore concentrate grains in the pellet, the fly-ash-based binders undergo a “pozzolanic” reaction with water and alkali materials to form a cementitious bond between particles. It was demonstrated that, while fly-ash-based binders used alone had performance comparable to performance of bentonite binders, combinations of fly-ash-based binder and bentonite performed poorly. This was because of the significantly different binding mechanisms for the two types of binder. In particular, soluble calcium ions that were needed for the fly-ash-based binder severely degraded the performance of bentonite.

Fly-ash is much more available than bentonite, and since it is generally considered to be a waste product from coal combustion, it is much less expensive as well. One of the features of fly-ash is that it often has a high content of unburned carbon, and fly-ashes with more than 6% carbon cannot be used as concrete admixtures, which is the current dominant market for fly-ash. This project confirmed that a high carbon content did not harm the performance of fly-ash-based binders in producing iron ore pellets, and in fact the presence of carbon provided a supplemental fuel source that could reduce the quantity of fuel that would need to be provided to fire the pellets. Since the fly-ash used could be material that has no other market, the use of fly-ash-based binders for iron ore pellet production is significantly more economical than the use of high-grade bentonite.

Novel Binders and Methods for Agglomeration or Ore

(US Dept of Energy, 10/1/2003-12/31/2006)

In agglomeration of iron ore to produce pellets for use in the blast furnace and in advanced ironmaking processes, it is important to determine the effects of water chemistry on the performance of bentonite clay binders and how this impacts the pellet quality. It was determined that the water that remains in the filter cake after filtration in iron ore concentrators can contain several hundred times greater concentrations of calcium ions and other cations, due to surface chemical effects carrying the ions along with the water. This is a serious concern for pellet quality, as calcium ions are known to degrade the performance of bentonite clay binders. Based on the theory of the electrical double layer, it was predicted that reducing the pH of the solution to near the isoelectric point (IEP) of the magnetite particles would cause the bulk of the positively-charged calcium and magnesium ions to be released. Carbon dioxide injection was found to be the best available method for reducing slurry pH to near the magnetite IEP so that calcium and magnesium ions would be removed during filtration. In both laboratory and plant studies, the carbon dioxide injection produced the significant additional benefit of increasing filtration rates by up to 23.7%.

In iron ore pelletization, filtration costs are in the range of $0.60 - $1.50/ton, much of which is for the energy to apply vacuum to the system. The energy-efficiency benefits of the 23% increase in filtration rate would be adequate justification for carbon dioxide injection, even in the absence of effects on pellet quality. Improved binder technology will also allow the adoption of advanced single-stage ironmaking technologies, which are approximately 13% more energy-efficient than the conventional pelletization-blast furnace technology. Assuming that 50% of the industry converts to single-stage ironmaking, this will save an estimated $6.51*10^{13}$BTU/year.

Temperature and Viscosity Effects in Mineral Comminution Circuits

(U. S. Bureau of Mines and Dow Chemical Company, 9/1/1982-9/30/1993)

It was observed by an operating iron ore concentrator that there were significant seasonal variations in grinding mill efficiency, with the efficiency being degraded during the coldest winter months. It was unknown whether this loss of efficiency was due to changes in the fracture resistance of the rocks themselves as they were chilled, or due to changes in properties of the mineral slurry in the grinding mill.

Extensive examinations of operating plant data confirmed that there was a correlation between specific grinding energy and the temperature of the mill slurry feed, with grinding energy increasing up to 18% in the winter months. "Drop test" studies were carried out to determine whether frozen ore had a greater resistance to fracturing than room-temperature ore. In these experiments, ore samples that had been adjusted to the desired temperature were dropped a height of 20 feet onto a steel plate, and the degree of fracturing was measured. It was found that dry ore pieces had the same fracture resistance regardless of whether they were frozen or unfrozen, while porous rocks that were saturated with water were considerably more fracture-resistant when they were frozen. Since the iron ore had very low porosity, there were no changes in ore fracture resistance that could have caused the observed increase in grinding energy.

Laboratory grinding experiments confirmed that there was a variation in grinding efficiency with temperature. A system was developed for measuring the viscosity of mineral slurries with the advice of personnel from Dow Chemical Co., and it was determined that chilling of the slurry caused an increase in viscosity that in turn increased the energy required for grinding. It was also determined that viscosity increases due to lowered temperature changed the separation performance of hydrocyclone classifiers that are used for size control in the grinding circuit.

To confirm these results, pilot-scale experiments were carried out using an instrumented autogenous grinding mill (6 feet in diameter x 2 feet long), grinding chilled and unchilled ore. Again, a good correlation was found between temperature, viscosity, and grinding energy. An additional effect was also noted, where very cold ore coming in contact with chilled water could freeze a layer of ice around the ore pieces, which could freeze ore to the side of the mill briefly and prevent it from being ground.

Based on the results of this project, the iron ore concentrator has taken measures to control temperature of their mill slurry in the winter, and grinding efficiency has been improved.

Optimization of Comminution Circuit Throughput and Product Size Distribution by Simulation and Control

(US Dept of Energy, 12/20/2000-7/31/2005)

Grinding mills in iron ore concentrators are major users of energy, and it is estimated that only 1-2% of this energy is actually used to generate new particle surfaces, with the rest dissipated as noise and heat. There is therefore tremendous scope for improving energy efficiency of grinding. Given the poor energy efficiency of grinding, it is particularly important that ore not be ground to any finer size than is strictly necessary. However, iron ore concentrators that use hydrocyclones for size control in their grinding circuits suffer from a problem where the high-density iron oxide particles are retained in the circuit at a finer size than the lower-density particles of gangue minerals. Therefore, in order to grind to a sufficiently fine size that the gangue can be separated from the iron oxides, the iron oxides must be "overground" to a size finer than necessary.

In this study, it was determined that overgrinding of iron oxides was wasting a considerable amount of energy, with almost 30% of the feed to the grinding mill consisting of recycled fines that should have been removed from the circuit. So, alternative grinding circuit designs were developed and simulated to determine how best to reduce overgrinding without degrading the overall plant performance. Studies with the hydrocyclone showed that there was no feasible way to use a single stage of hydrocycloning to reduce the tendency to retain the high-density iron oxides. However, plant operating data provided by the industrial co-sponsor showed that two-stage cycloning could be used to generate three products: (1) a coarse stream where all the particles needed to be recycled for further grinding; (2) a fine stream where all of the particles were small enough to be removed as final product; and (3) a narrowly-sized intermediate stream that required only a small amount of further grinding to reach the target size.

Simulations of the circuit showed that the intermediate stream could be sufficiently ground in a single pass through a grinding mill, with no need to classify it again by hydrocycloning after that single pass of grinding. Since this stream contained all the particles that would normally be retained and overground by the circuit, this eliminated the major source of grinding inefficiency. It was estimating that incorporating this change into the circuit could reduce circulating loads from 250% to only 42%, allowing the capacity of the circuit to be increased by 50% without using any additional grinding energy.

Bacterial Extraction of Phosphorus from Iron Ore

(U. S. Dept. of Energy, 10/1/1992-4/30/1993)

Phosphorus is a problem in ironmaking feedstocks, as phosphorus in iron gives the metal undesirable properties. Some iron ore sources have significant levels of phosphate minerals that are difficult to remove, and so use of ore from these sources requires the iron and steel plants to remove the excess phosphorus from the molten metal.

If phosphorus can be removed from the ore at the ore concentrator, the value of the iron ore concentrate can be increased. While phosphate minerals are difficult to separate from iron oxides using conventional physical separation techniques, it is possible that they could be removed by a sufficiently low-cost selective dissolution process.

In this project, microorganisms were used to selectively dissolve phosphate minerals from iron ore. Since microorganisms require phosphorus as a critical nutrient, many of them have developed the ability to dissolve phosphate minerals from ore, and so growth of these organisms on iron ore is expected to be able to solubilize and remove the phosphates.

Experimental "proof of concept' work was carried out with a variety of microorganisms to determine their phosphorus removal capability. Certain filamentous fungi, which secrete organic acids that dissolve phosphate minerals, were found to be most effective. The method could remove phosphorus, but the currently known organisms have low growth rates, and as a result it requires several weeks for phosphorus to be removed.

If faster-growing organisms can be discovered or developed, this technology has good potential for reducing the phosphorus levels of high-phosphate iron ores.