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(2-01) p.1 of 2

UNITED STATES DEPARTMENT OF ENERGY (DOE)
Announcement of Scientific and Technical Information (STI)
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OMB CONTROL NO.
1910-1400

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B. Recipient/Contractor
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Enrichment of By-Product Materials from Steel Pickling Acid Regeneration Plants (TRP 9942)

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E. STI Product Issue Date/Date of Publication
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G. STI Product Reporting Period
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I. Subject Categories *(list primary one first)*
32 Energy Conservation, Consumption and Utilization
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J. Description/Abstract

A new process for manufacturing an enriched, iron-based product (Strontium Hexaferrite) in existing steel pickling acid regeneration facilities was evaluated. Process enhancements and equipment additions were made to an existing acid regeneration plant to develop and demonstrate (via pilot scale testing and partial-capacity production trials) the viability of a patented method to produce strontium-based compounds that, when mixed with steel pickling acid and roasted, would result in a strontium hexaferrite powder precursor which could then be subjected to further heat treatment in an atmosphere that promotes rapid, relatively low-temperature formation of discrete strontium ferrite magnetic domains yielding an enriched iron-based product, strontium hexaferrite that can be used in manufacturing hard ferrite magnets.

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L. Recipient/Contract Point of Contact *Contact for additional information (contact or organization name To be included in published citations and who would Receive any external questions about the content of the STI Product or the research contained herein)*
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REPORT DOCUMENTATION PAGE

Title and Subtitle:

AISI/DOE Technology Roadmap Program for the Steel Industry

Enrichment of By-Product Materials from Steel Pickling Acid Regeneration Plants [TRP9942]

Author:

Lu Swan, Principal Investigator, Delta Ferrites LLC

Performing Organization

Bailey-PVS Oxides LLC, Canonsburg, PA

Abstract

A new process for manufacturing an enriched, iron-based product (Strontium Hexaferrite) in existing steel pickling acid regeneration facilities was evaluated. Process enhancements and equipment additions were made to an existing acid regeneration plant to develop and demonstrate (via pilot scale testing and partial-capacity production trials) the viability of a patented method to produce strontium-based compounds that, when mixed with steel pickling acid and roasted, would result in a strontium hexaferrite powder precursor which could then be subjected to further heat treatment in an atmosphere that promotes rapid, relatively low-temperature formation of discrete strontium ferrite magnetic domains yielding an enriched iron-based product, strontium hexaferrite that can be used in manufacturing hard ferrite magnets.

The primary objective, to demonstrate the viability of manufacturing an enriched, iron-based product (Strontium Hexaferrite) at an existing steel pickling acid regeneration facility was successfully achieved. It was proven during co-roasting pilot-scale trials, that strontium could be added to the spray roaster without adversely affecting the quality of regenerated acid. A partial-capacity post heat treat trial resulted in a magnetically acceptable ferrite powder. A new potential beneficial energy saving discovered during plant trials shows that agglomeration of the co-roasted admixture in the spray roaster greatly increases the particle size of the admixture by more than threefold, compared to the particle size of iron oxide. This reduction in surface area of the admixture, compared to iron oxide, will result in less water necessary to slurry and pump the admixture to the post heat treat calciner. Despite the lack of repeatability for Fe and Sr content (measured by Inductively Coupled Plasma), and the extremely high chloride content in the resulting co-roasted powder, the ability to produce large quantities of a Strontium enriched Iron Oxide precursor, and further post heat treat same through a calciner, was demonstrated.

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AISI/DOE Technology Roadmap Program

Final Report

TRP 9942 – Enrichment of By-Product Materials from Steel Pickling Acid Regeneration Plants

By

Lu Swan

September 2009

Work Performed under Cooperative Agreement
No. DE-FC36-97ID13554

Prepared for
U.S. Department of Energy

Prepared by
American Iron and Steel Institute
Technology Roadmap Program Office
Pittsburgh, PA 15222

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1.0 Executive Summary

A new process for manufacturing an enriched, iron-based product (Strontium Hexaferrite) in existing steel pickling acid regeneration facilities was evaluated. Process enhancements and equipment additions were made to an existing acid regeneration plant to develop and demonstrate (via pilot scale testing and partial-capacity production trials) the viability of a patented method to produce strontium-based compounds that, when mixed with steel pickling acid and roasted, would result in a strontium hexaferrite powder precursor which could then be subjected to further heat treatment in an atmosphere that promotes rapid, relatively low-temperature formation of discrete strontium ferrite magnetic domains yielding an enriched iron-based product strontium hexaferrite that can be used in manufacturing hard ferrite magnets.

The primary objective, to demonstrate the viability of manufacturing an enriched, iron-based product (Strontium Hexaferrite) at an existing steel pickling acid regeneration facility was successfully achieved. It was proven during co-roasting pilot-scale trials, that strontium could be added to the spray roaster without adversely affecting the quality of regenerated acid. A partial-capacity post heat treat trial resulted in a magnetically acceptable ferrite powder. Despite the lack of repeatability for Fe and Sr content (measured by Inductively Coupled Plasma), and the extremely high chloride content in the resulting co-roasted powder, the ability to produce large quantities of a strontium enriched iron oxide precursor, and further post heat treat same through a calciner, was demonstrated.

Future plans may involve continuing partial-capacity production trials and potentially implementing process improvements with trials to ameliorate any material problems experienced during trials. Issues regarding higher temperature requirements in the spray roaster and the inconsistency of the chemistry would likely need to be addressed and potentially overcome to realize commercial viability.

Production of strontium hexaferrite (SrFe12O19) magnetic powder through this innovative process is envisioned to provide significant functional and economic advantages to the magnetic industry over the presently employed traditional methods of production and will benefit all steel production facilities with steel pickling output and could have applications in the automotive and appliance manufacturing industries.

2.0 Overall Goal

To develop and demonstrate, via pilot-scale testing and partial-capacity production trials, a new process for the manufacture of an enriched, iron-based product (strontium hexaferrite), through the use of existing steel pickling acid regeneration facilities.

3.0 Research Objectives

- Develop and demonstrate an enrichment technology for the recycling of iron-bearing by-products from steel pickling operations.
- Develop and demonstrate, on a partial-capacity scale, the production viability of producing enriched magnetic-type (ferrite) powders utilizing waste iron by-products.
- Provide an improved means of producing the products in an energy efficient and environmentally improved manner.
- Produce value-added materials from recycling by-product iron oxides, and establish an effective means of producing magnetic powder to benefit both the domestic steelmaking and ferrite industries.

4.0 Background

Finishing processes clean the surface of semi finished, hot-rolled steel products prior to cold rolling, forming, and/or coating operations. Acid pickling is a common finishing process that chemically removes mill scale, rust, oxides, oil, grease, and soil from the surface of the steel. In continuous pickling processes, the steel is immersed in acid cleaning tanks containing hydrochloric, sulfuric, or a combination of various pickling acids and then cleaned in a series of water rinsing tanks. Alkaline cleaners may also be used to remove contaminants from the steel surface.

Some by-products in spent pickling liquor include iron-bearing materials that could be used in the production of magnetic powder products. Bailey-PVS Oxides, LLC [BPO] lead a project to enhance the recovery of these iron-bearing by-products, which will help the steel industry reduce wastes, save energy, and provide a new value-added product for the U.S. magnetics industry.

Currently, the magnetics industry purchases various feedstock powder components that are individually produced, cooled, packaged, and transported. Strontium hexaferrite powders produced at existing acid regeneration plants would simplify magnetic powder production, providing significant economic benefits to all steel production facilities with steel pickling output and could have applications in the automotive and appliance manufacturing industries.

Traditional co-Roasting Process:

Finishing processes clean the surface of semi finished, hot-rolled steel products prior to cold rolling, forming, and or coating operations. Acid pickling is a common finishing process that chemically removes mill scale, rust, oxides, oil, grease, and soil from the surface of the steel. In continuous pickling processes, the steel is immersed in acid cleaning tanks containing hydrochloric, sulfuric, or a combination of various pickling acids and then cleaned in a series of water rinsing tanks. Alkaline cleaners may also be used to remove contaminants from the steel surface. Some by-products in spent pickling liquor include iron-bearing materials that could be used in the production of magnetic powder products.

The steel plant pickling process has traditionally used hydrochloric acid (HCl) to chemically etch off surface oxides on steel. When the acid is spent the resulting solution is called spent pickle liquor (SPL), which is a form of ferrous or ferric chloride. The SPL is then sent to an acid regeneration plant where it is processed through a spray roaster to re-form HCl. The spray roaster mixes SPL with oxygen and water at specific temperatures to cause pyrohydrolysis. The end result is regenerated HCl acid and iron oxide. For example:

$$\mathbf{4FeCl_2 + 4H_2O + O_2 \rightarrow 2Fe_2O_3 + 8HCl}$$

$$\mathbf{2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl}$$

The regenerated HCl is then sent back to the steel pickling process. As illustrated in *Figure 1*, below, the hydrochloric acid fraction of the regeneration process exits the spray roaster as a vapor mixture, which is then condensed in the absorber yielding 17% to 18% regenerated acid. This regenerated acid is well suited for reuse in the pickling line process.

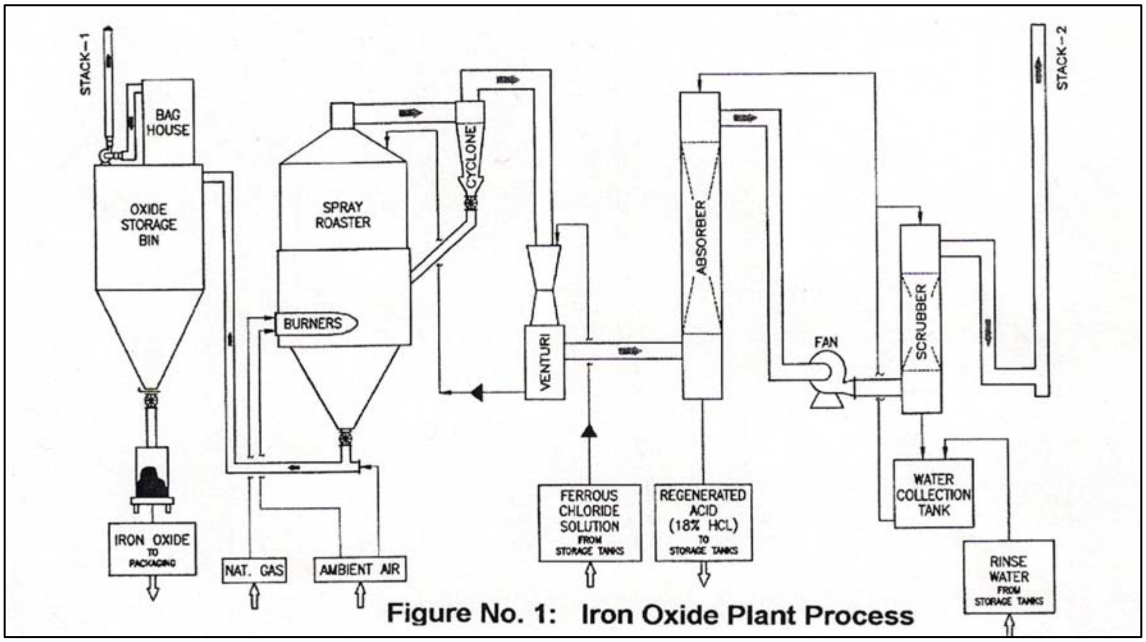


Figure No. 1: Iron Oxide Plant Process

The ferric oxide portion is precipitated and falls to the bottom of the spray roaster as a dry, finely divided, crystalline powder of high purity (99% Fe_2O_3). The iron oxide by-product is used primarily in pigment and magnetic/ferrite applications. The high purity and physical characteristics of the Spray Roaster produced iron oxide allows its use as the principal feedstock for the current manufacture of strontium and barium hexaferrites by the U.S. magnetics industry mainly for the production of hard ferrites. *Figure 2*, below, shows an aerial view of the Acid Regeneration plant in Delta, Ohio where the project took place.

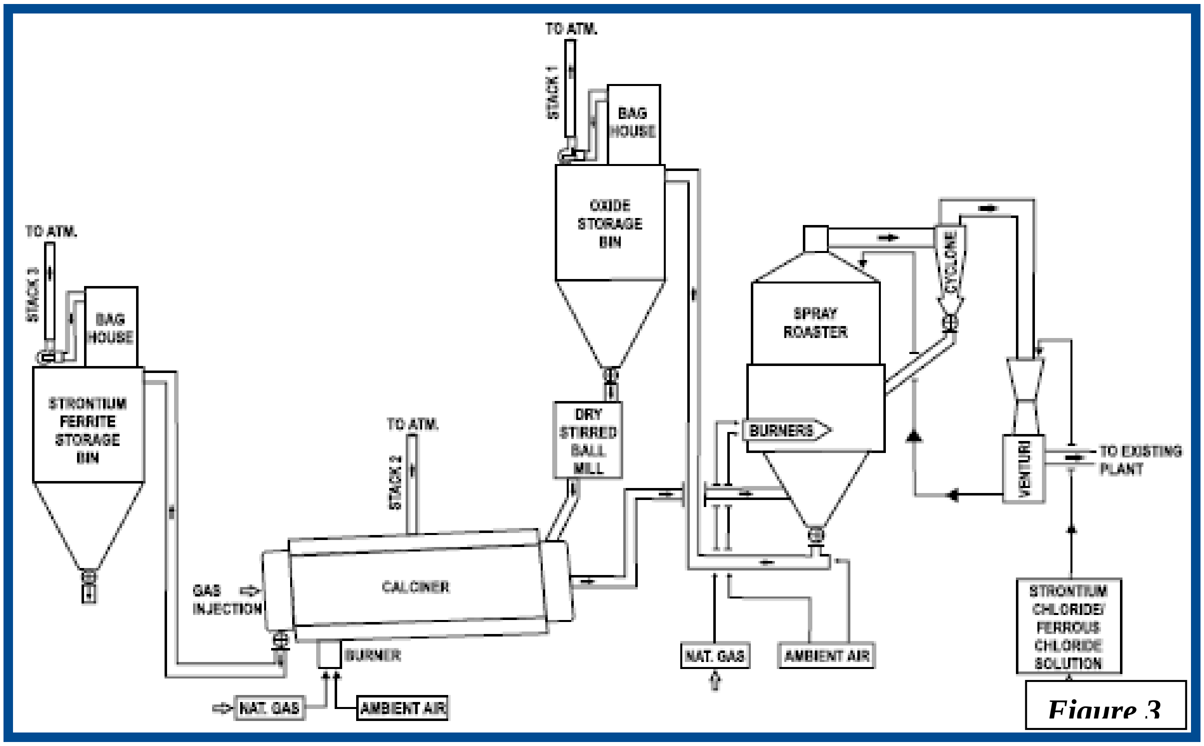
Figure 2: Aerial view of Acid Regeneration Plant in Delta, Ohio.

In the traditional process, both the iron oxide and strontium/barium feed stocks are individually produced, cooled, packaged, and transported to other processors as fine, non-flowable powders. These powders are mixed together in the proper proportions into a wet slurry, introduced into a high temperature kiln, and held at a temperature around 1200 C (2200 F) for several hours to produce the strontium or barium hexaferrite crystals sintered into marble-sized balls. The crude strontium or barium hexaferrite product is ground to a fine powder; the platy hexaferrite crystals are broken during this grinding process, thus degrading the magnetic characteristics of the resulting powder. The ferrite powder product is either pressed into defined shapes in the presence of a magnetic field then sintered to yield a hard “ceramic magnet” form, or shipped to magnetic component manufacturers. The ferrite powder is incorporated into polymer systems to produce, among many other “polymer-bonded magnetic products”, such as gaskets for refrigerator doors, and increasingly for automobile doors that provide a magnetic force to guarantee a seal when the door is closed.

When the wet slurry mixture of strontium carbonate and iron oxide is fired through a high temperature kiln, many intermediate diffusional crystal chemistry reactions take place. First, the strontium carbonate decomposes to strontium oxide and, second the high heat allows the softened almost-molten particles to become a homogeneous mass. Strontium atoms migrate throughout the iron oxide particles to achieve a ratio of 1 strontium atom in close proximity to 12 iron atoms. Strontium hexaferrite crystals, $SrFe_{12}O_{19}$ can then nucleate and grow. Acceptable product magnetic powder properties require that the strontium hexaferrite be composed of many small well-formed crystals. One of the challenges of this process is getting the strontium atom evenly dispersed throughout the mixture so that it is readily available for diffusion into the iron oxide at high temperatures. A typical band-aid to the problem is to add more heat resulting in a harder calcine which is more difficult to mill. As the milling gets more aggressive, it tends to destroy more of the ferrite crystals, lowering magnetic properties.

Innovative co-Roasting Process

Preliminary trials conducted by Bailey PVS Oxides (BPO) and Chemical Products Corp. (CPC) in 2003 confirmed the viability of producing strontium hexaferrite precursor powder directly from SPL while regenerating and recovering HCl for reuse.



Flow diagram of strontium hexaferrite magnetic powder production process

The new process (*Figure 3*), claimed in U.S. Patent 6,660,242 awarded to Chemical Products Corporation (CPC), combines, simplifies and significantly improves strontium ferrite production efficiency and strontium ferrite product quality over traditional production steps currently performed at disparate facilities. The strontium carbonate is transported to an existing acid regeneration plant and there reacted with the excess hydrochloric acid (instead of the present practice of spray-roasting a solution containing only ferrous chloride) in the SPL feed to the Spray Roaster yielding soluble strontium chloride in the ferrous chloride solution. The iron ions and strontium ions present in the same solution precipitate in an intimately admixture on an atomic level in the Spray Roaster. The relative proportions of iron and strontium are controlled resulting in a strontium hexaferrite powder precursor composed of iron and strontium oxides and chlorides which are then subject to further heat treatment in an atmosphere that promotes rapid, relatively low-temperature formation of discrete strontium ferrite magnetic domains. Unlike the traditional ferrite production process, hexaferrite crystal size can be controlled to yield optimum magnetic properties and sintering of the crystals into a hard mass is avoided because high temperature migration of strontium into ferric oxide particles is unnecessary.

The new process differs from the traditional process of making strontium ferrite primarily because the strontium atom goes through the spray roaster at the same time as the iron atom resulting in perfectly dispersed strontium throughout the iron oxide. It also results in very similar particle sizes of strontium to iron. These two effects promote better solid state diffusion of the strontium into the iron oxide and should allow the diffusion to take place during the post heat treat step at lower temperatures. Lower temperature post heat treat could result in a softer, less dense calcine which would mill easier and faster, requiring fewer passes through the mill to achieve required particle size, potentially using less energy. Less milling will also result in a higher magnetic property, as milling tends to destroy the ferrite crystals.

Production of strontium hexaferrite ($SrFe_{12}O_{19}$) magnetic powder through this innovative process is envisioned to provide significant functional and economic advantages to the magnetic industry over the presently employed traditional methods of production and will benefit all steel production facilities with steel pickling output and could have applications in the automotive and appliance manufacturing industries.

Preparation Toward Research Objectives:

A preparation area, *Figure 4* was installed to incorporate the Spent Pickle Liquor (SPL) with the Strontium Carbonate. The strontium preparation area (SPA) involves a brick lined mix tank with agitation in order to mix the SPL with the Strontium Carbonate. Pump lines and pumps were installed to get the SPL into the tank. A bulk bag unloader with conveying screw and bucket elevator were installed get the Strontium Carbonate into the tank.

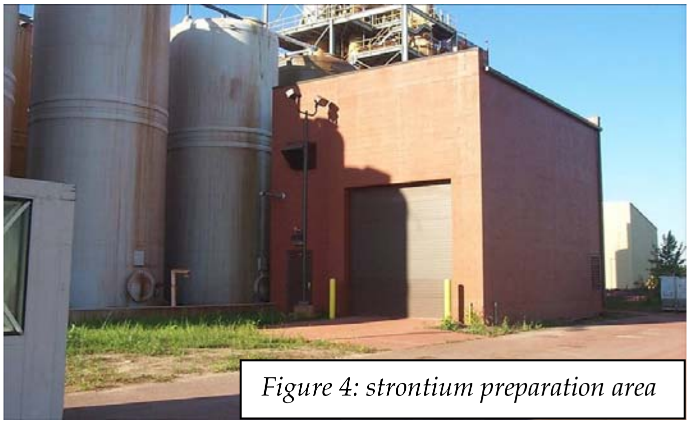


Figure 4: strontium preparation area

Figure 5: Mixing and Conveying Equipment

The out gassing from the tank was ducted to the scrubber for the spray roaster, and a dust collector was installed to vent the mix tank. A large fiberglass storage tank, and feed lines to the spray roaster, was installed to store and feed the admixture. Programmable Logic Controller and weighment controls were incorporated to operate the equipment. Figure 4 shows the outside of the SPA building and the fiberglass storage tank. *Figure 5* shows the equipment for the SPA.

A building was constructed for the post heat treat equipment (*Figure 6*). Raw material hoppers and conveying equipment was installed. Two mix tanks with agitation were implemented to slurry the precursor powder. A large holding tank with agitation was later installed to hold a buffer of slurry to feed to the calciner. Pump over pumps for transferring slurry from the mix tanks to the feed tank were implemented, as well as a pump to feed the calciner. A water cooled feed tube was installed inside the calciner to allow the slurry to enter the feed end.

Figure 6: Post heat treating facility

Figure 7

A 60 ft long calciner was implemented as can be seen in *Figure 7*. The calciner was brick lined on site as shown in *Figure 8*. *Figure 7* also shows the cooling tube for the calciner, conveying equipment, and storage hopper for the clinker. A conical ball-mill with air swept classification was installed to grind the clinker down to the proper size for ferrite usage. Lastly, a powder storage hopper and powder bagging station with scale weighment was installed as the final step in the process.

Fiscally sound decisions were made to buy used equipment (sized to match the output of the spray roaster) because it was substantially less than new equipment. Otherwise, proper partial capacity-scale production trials would have been impossible, and the trial phase would have resulted in a tremendous amount of waste.

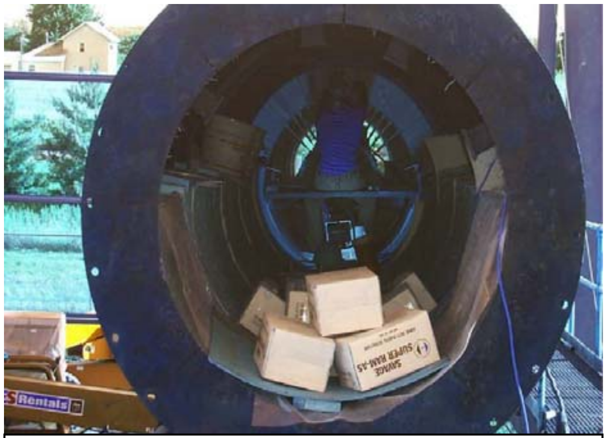


Figure 8: Construction Phase of Lining the Calciner with Refractory Brick.

Once the SPA equipment was in commissioned in April 2007; trials commenced. Two large scale co-roasting trials took place in April 2007 and September 2008 (Post heat-treat equipment was commissioned in October 2008). Due to an equipment breakdown, the September 2008 trial was completed in February 2009 and a production trial through the calciner and ball mill was conducted in August 2009 using the February 2009 co-roasted material.

5.0 Research Progress:

- ***Develop and demonstrate an enrichment technology for the recycling of iron-bearing by-products from existing steel pickling operations.***

Using Strontium Preparation Area (SPA); produced a total of 37,000 gallons of SPL enriched with Strontium admixture. The entire 37,000 gallons was ultimately co-roasted through the existing acid regenerating spray roaster. The resulting Strontium enriched Iron Oxide precursor was collected for future processing through the post heat treatment facility and milling process.

Proved the admixture could be processed through an existing acid regeneration plant without any adverse affects on the regenerated acid. All quality tests on co-roast produced acid indicated it to be within specification. All acid regenerated during co-roasting trials was shipped back to the steel plants with no reported problems.

- ***Develop and demonstrate, on a partial-capacity scale, the production viability of enriched magnetic-type (ferrite) powders utilizing waste iron by-products.***

Successfully demonstrated the viability of producing magnetically acceptable ferrite powder by a new process at an existing steel pickling acid regeneration facility.

During plant trials, two main technical challenges arose; 1.) the lack of repeatability of the Fe and Sr content measured by Inductively Coupled Plasma, and 2.) the extremely high chloride content of the co-roasted powder. However, a short post heat treat trial resulted in a ferrite powder whose quality was magnetically acceptable.

- ***Provide improved means of producing the products in an energy efficient and environmentally improved manner.***

The original projected energy savings related to the consolidation of supply chain involve:

a) elimination of fuel usage to ship the iron oxide to a ferrite production facility;
b) elimination of super sacks due to the admixture being pneumatically transferred directly to an onsite ferrite production facility;
c) reduced labor due to the elimination of packaging;
d) no disposal costs of the super sacks/pallets; and
e) elimination of in-plant transfer forklifts.

A new potential beneficial energy saving discovered during plant trials shows that agglomeration of the co-roasted admixture in the spray roaster greatly increases the particle size of the admixture by more than threefold, compared to the particle size of iron oxide. This reduction in surface area of the admixture, compared to iron oxide, will result in less water necessary to slurry and pump the admixture to the post heat treat calciner.

Incremental energy savings are expected due to the fact that less heat and time will be required for the solid state diffusion reaction which is necessary to form ferrite. The initial calciner trial was too short to prove this. Once the high chloride problem is solved, longer calciner trials will be possible. It is obvious to the author that the strontium and the iron atoms will essentially have very similar physical particle size, as well as near perfect dispersion of the strontium, and will therefore, diffuse at lower temperatures and in less time in the post heat treat calciner. Lower temperatures in the calciner should also result in less energy to ball mill the final product.

Less fugitive emissions will result from the anticipated reduction in new material processing and handling operations. Emissions (particulate and combustion gas) from calcining operations will be reduced as a result of reduced operating times. Particulate emissions will also be eliminated by the discontinuation of the use of various product handling operations such as the conveying of raw materials, dry mixing operations, stockpile material movement, and the like.

Additional energy savings may be quantified in any future plant trials.

- ***Produce value-added materials from recycling by-product iron oxides, and establish an effective means of producing magnetic powder to benefit both the domestic steelmaking and ferrite industries.***

Overall, an acceptable ferrite powder was produced using the new method. Problems with inconsistent Fe and Sr measurements and high chlorides of co-roasted powder need to be resolved, for commercial viability.

It is expected that ferrite powders produced with this new method will be a significant improvement over current materials. The powders are expected to be of higher magnetic quality and produced at lower costs.

6.0 Conclusions

The primary objective, to demonstrate the viability of manufacturing an enriched, iron-based product (Strontium Hexaferrite) in an existing steel pickling acid regeneration facility was successfully achieved. It was proven during co-roasting pilot-scale trials, that strontium could be added to the spray roaster without adversely affecting the quality of regenerated acid. A partial-capacity post heat treat trial resulted in a magnetically acceptable ferrite powder. Despite the lack of repeatability for Fe and Sr content (measured by ICP), and the extremely high chloride content in the resulting co-roasted powder, the ability to produce large quantities of a Strontium enriched Iron Oxide precursor, and further post heat treat same through a calciner, was demonstrated.

The lack of uniform repeatability of Fe and Sr content when measured by ICP problem most likely lies in the preparation of the samples; ongoing improved sample prep procedures may reduce the variations. Once the repeatability issue is resolved, the next technical challenge will be to develop real-time tests that would allow fast enough results for any future long-term partial production trials that may be conducted [outside of this project].

The chlorides resulting from the spray roaster co-roast powder were too high for extensive post heat treatment trials through the calciner due to its limited ability to handle the corrosion such high chlorides would create. The author believes that the spray roaster temperatures are insufficient for SrCl to go through pyrohydrolysis. The top and mid temps in the existing roaster are approximately 750 F and 1600 F respectively. Unfortunately, there is no data for the required temps for SrCl to pyrohydrolize; however, there is data for MgCl when producing MgO using the spray roaster process. The literature reports these temperatures to be 900F top and 1850F mid temps. Sr is in the same chemical family of alkaline earths as Mg, and has a higher atomic number; therefore it is estimated that SrCl would require a top temp of 1000F and mid temp of 2000F for pyrohydrolysis to occur.

The main achievements of this project were threefold. First, the Strontium Prep Area (SPA) was successfully installed which allowed the introduction of strontium into the spray roaster. Second, large scale co-roasting trials proved that the strontium addition did not have any adverse affects on the quality of the regenerated acid. The co-roasting trials also resulted in a strontium enhanced powder with a much larger particle size compared to the iron oxide from traditional spray roasting, which will allow a reduced amount of water required during the post heat treat translating into a direct fuel savings. Third, post heat treat equipment was successfully installed, and a short post heat treat trial produced a magnetically acceptable ferrite powder.

Problems due to lack of uniform chemistry repeatability, extremely high chloride contents, and recurring post heat-treat equipment breakdowns prevented long-term partial-capacity production trials and remain technical hurdles to be overcome for commercial use.

7.0 Future Plans and Technical Barriers to be overcome

This project has been completed. There remain technical issues to be overcome to realize commercial viability which may be addressed by one or more of the project participants in the future. Future plans may involve continuing partial-capacity production trials and potentially implementing process improvements with trials to ameliorate any material problems experienced during trials. Issues regarding higher temperature requirements in the spray roaster and the inconsistency of the chemistry would likely need to be addressed and potentially overcome to realize commercial viability.

One of the most important technical challenges will be to increase the temperature capability of the spray roaster in order to allow pyrohydrolysis of the strontium chloride. This could be attempted by adding more spray bars to the quench section of the spray roaster exhaust stream. More quenching should allow higher temperatures in the spray roaster and still not destroy heat sensitive downstream equipment. In parallel, it needs to be determined if the brick lining in the spray roaster can handle the additional temperatures. Also, the capacities of the burners in the spray roaster need to be confirmed for the high temperature requirement.

Sample preparation procedures for the ICP should be evaluated. An analytical laboratory should be consulted to aid in this effort. Repeatability must be analyzed and proven before conducting subsequent trials. Once the spray roaster temperature optimization and high chloride problem of the admixed precursor is solved, it may be possible to run the precursor powder through post heat treatment, at which time higher product volumes could be processed allowing for longer trial runs and making it possible to fully validate projected energy savings.

8.0 References

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