



Low Temperature Electrolysis of Mixed Metal Oxides

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Abstract

This project tested the synthesis of mixed metal oxides and the reduction of those oxides to metal alloy powders via Low Temperature Electrolysis (LTE). Starting with the synthesis of a mixed metal oxide via Evaporative Decomposition of Solutions (EDS), a number of solutions were tested for use as the electrolyte in the electrolytic cell. Multiple trials demonstrated that the use of a 50-60 wt% sodium hydroxide solution for the electrolyte was an integral factor in the successful reduction of an oxide.

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Executive Summary

This project looked at the use of low temperature electrolysis (LTE) to reduce a mixed metal oxide into a complete metal alloy. Previous experiments had shown that multiple transition metals could be converted from an oxide to the metallic form, indicating a possible replacement for the standard metal refining process of heating the metal oxide in a blast furnace to 1000-1200°C. This process used an electrolyte solution at 100°C combined with low voltage electric current to reduce the oxide. The hope is that LTE can one day be used to replace the current high temperature process as a safer and less energy intensive method to refine metal ores.

LTE of a mixed metal oxide was performed in two steps. First a mixed Fe/Ni nitrate was prepared via Evaporative Decomposition of Solutions (EDS) process, then the mixed nitrate was calcined at 750°C to obtain a mixed iron/nickel oxide. Composition of the mixed oxide was confirmed via X-ray Diffraction (XRD). This mixed oxide was then prepared via the same method as the pure metal oxide had been in previous experiments, and was run through the LTE cell with varying electrolyte solutions to determine if a complete metal alloy could be obtained by the LTE process. The final product of electrolysis was then analyzed via XRD to determine whether or not the mixed oxide had been reduced.

Table of Contents

Abstract	1
Acknowledgements	2
Executive Summary	3
Introduction	5
Background	6
Methodology	11
Results	15
Analysis	17
Conclusions and Further Research	22
References	23
Appendix I	24

Introduction

This report contains the research conducted by Baker, Bonefas, Kyer, and Morneau concerning the reduction of metal oxides and mixed metal oxides. Background information concerning low temperature electrolysis and mixed metal oxide synthesis can be found in the following section, followed by the research conducted from September 2016-March 2017. Additionally, conclusions about the data as well as recommendations for future research are provided.

Background

Electrolysis is a technique that converts a metal oxide into the metallic form by applying an electric current. The oxide is placed between two electrodes and submerged in an electrolyte. Types of electrolysis include high temperature electrolysis (HTE), requiring temperatures as high as 1000°C, and molten oxide electrolysis (MOE), involving the production of a metal in the liquid state. MOE is beneficial because it does not have a carbon byproduct, so it does not emit any greenhouse gases (GHG). However, because the reaction takes place around temperatures of 1500°C it is difficult to find an inert anode that does not oxidize. Hydrogen flash smelting (HFS) is a promising method of electrolysis, utilizing gas-solid flash reduction at 1200°C to reduce the metal. This method is not commonly used due to the high cost of hydrogen. Compared to these forms of electrolysis, low temperature electrolysis (LTE) uses temperatures around 100°C to achieve the same reduction of an oxide, but with far less energy input to heat the reaction.¹ LTE is currently being researched as a possible alternative for refining metal ore into a useable metallic form.

The current practice for refining of metals starts with the mining process. The majority of deposits of most transition metals are found in the form of metal oxides underground. The ore that contains the desired metal is extracted via blasting, drilling, or other means, and then is transported to processing plants for refining. A number of chemical and physical methods are used to purify the ore to extract the metal oxide from the other contaminants, before the metal oxide is sent along to be further processed into a metallic form.

¹ Wang, Q., Zhu, Y., Qiuyang, W., Gratz, E., Wang, Y. *Low temperature electrolysis for iron production via conductive colloidal electrodeI*: RCS Advances, 2014. Print.

The presently used methods to convert the oxide of transition metals into the metallic form most often involve very high temperatures, and therefore a large input of energy. The most common method for refining metals like iron, copper, and silver is carbothermic reduction, more commonly known as smelting. This multi-stage process involves first “roasting” the metal ore by heating it in an oxidizing environment to fully convert the metal to the oxide form. This pure oxide is then converted to the final metallic form by heating in a blast furnace to a much higher temperature, often over 1000°C, in a reducing environment. The reducing agent used is most often carbon monoxide, formed by the incomplete combustion of the fuel that heats the furnace.

The main problems with smelting are the extreme heat requirements and the environmental impact. Iron reduction requires temperatures of over 1200°C, which in turn requires a large amount of fuel to be burned to generate that heat. Coal is one of the most common sources of fuel, however burning coal releases numerous toxic emissions, including lead, mercury, and arsenic. In addition, the carbothermic reduction of iron and many other metals converts carbon monoxide into carbon dioxide, which is then released into the atmosphere. For every ton of crude iron produced, the process generates two tons of carbon dioxide, the gas that accounts for 80% of the United States’ greenhouse gas emissions. In addition, the process can release unreacted carbon monoxide, a greenhouse gas that is far more toxic to humans.

Another method of producing oxides is called evaporative decompositions of solutions (EDS). Powders used for EDS are most frequently single-component such as Fe_2O_3 and MgO , however, binary and ternary oxides have been prepared as well.

The apparatus used for EDS consists of a vertically mounted tube furnace with a high-purity mullite furnace tube. Co-Mo mixed oxides were prepared by first completely

dissolving the Molybdenum salt at 50°C, and then adding the Cobalt salt with continuous stirring. The total metal ion concentration prepared for each solution was 0.6M. Using a 316 stainless steel air-driven atomizer and pressurized liquid feed system the solution was introduced to the tube furnace. The center of the tube furnace was measured to be 700°C, which is where the decomposition reaction took place. 700°C was the chosen temperature because it was approximated to be the lower limit needed to ensure a complete decomposition of the salts.

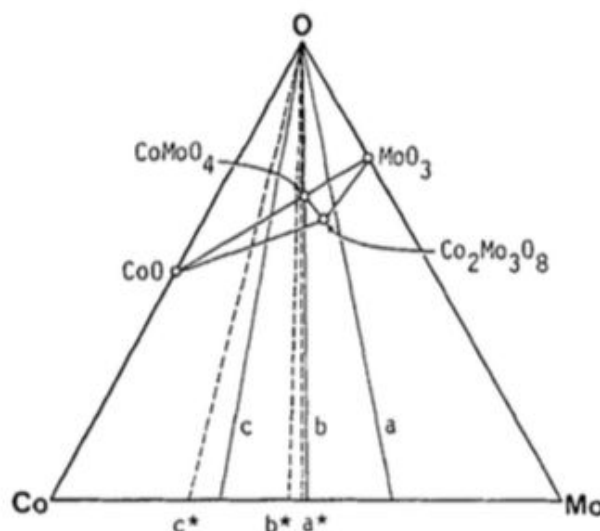


Fig. 1. Mo-O phase diagram at 700°C. Lines (a), (b), and (c) represent lines of constant Co/Mo ratio for precursor solutions. Lines (a*), (b*), and (c*) represent the corresponding measured Co/Mo ratio for the product oxides.²

The air that would be carrying the solution was preheated to 350°C, and then the droplets were dropped through the tube furnace. The reactor contact time is estimated to be about 2.5 seconds, after which the contents were collected using a scrubber. Finally the product was filtered, washed, and dried.

² Rossetti, G., Burger, J., Sisson, R. *Characterization of Mixed Cobalt-Molybdenum Oxides Prepared by Evaporative Decomposition of Solutions*: J. Am. Ceram. Soc., 1989. Print.

Upon analyzing the resulting product, it was found that the reactivity of the Co-Mo were sufficient enough for secondary solid-state decomposition reactions to take place following the decomposition of salt.

One of the most significant parameters during LTE is the bell voltage. This voltage is responsible for determining the heat as well as the energy balance for the cell.³ In most cases, during electrolysis the cell voltage change is determined by the anode. Important parameters of the anode include the thickness, structure, and electrical conductivity of anode scale. The fluctuation and value of the voltage are necessary to determine the stability of LTE. Another less critical parameter of the LTE process is the current efficiency. Due to the structure and design of the electrolytic cell, it often does not provide material or electrical flows of notable quality. Currently, enough knowledge about LTE exists, allowing for the successful testing of new materials for inert anodes. Many elements on the periodic table are compatible with the LTE process.

Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At

Fig. 2. Elements that can be produced using LTE (in green)

Low temperature electrolysis requires significantly lower temperatures than smelting, resulting in a lower required energy input. The use of LTE to reduce newly mined metal oxides into a useable metal product would represent a significant step forward in metal refining, and

³ Redkin, A., Apisarov, A., Dedyukhin, A., Kovrov, V., Zaikov, Y., Tkacheva, O., Hryn, J. *Recent Developments in Low-Temperature Electrolysis of Aluminum*: ECS Transactions, 2012. Print.

allow a major reduction in greenhouse gas emissions caused by the refining industry. The reduction in usage of fuels like coal would also help reduce the volume of toxic nitrogen and sulfur oxides released into the atmosphere.

Methodology

Before experimenting with the possibility of creating new metal alloys via LTE, an experiment was setup to replicate the results of LTE for the production of iron. This process would be used to reduce Fe_2O_3 .

One gram of Fe_2O_3 was combined with 2 grams of carbon powder and placed in a ball mill overnight, yielding a fine homogeneous powder. The electrolyte was made by preparing a solution of 50 wt% NaOH. The mixed Fe_2O_3 was then applied to a titanium disk, having an area of approximately 1.2cm^2 . Titanium was chosen as the current collector for the cathode due to its low catalytic activity towards H_2 evolution. A polyethylene separator was applied to cover the colloid, preventing it from leaking into the liquid electrolyte. Two electrodes were then inserted into the solution through the top of the electrochemical cell. The assembly was placed into the solution and was then heated to about 100°C . In order to control the voltage that would be run through the sample at this temperature, Potentiostat was used. This program allowed for a voltage of 1.7 V to be run through the Fe_2O_3 at the optimal time; when the sample was approximately 100°C . The electrolysis took 5 hours, after which the electrochemical cell was cooled. The product was collected from the cell, was washed with water, and then again with ethanol. The sample was placed in an oven at 70°C until dry.

The dry sample was analyzed via x-ray diffraction. The results were nearly identical to the previous experiment, with XRD confirming that the Fe_2O_3 was reduced to metallic iron via LTE.



Fig. 3. Image of an open electrolytic cell, showing the platinum foil

Synthesis of the mixed metal oxide starting material was conducted via Evaporative Decomposition of Solutions (EDS). Nitrate salts of the two chosen metals were combined and dissolved in water to yield an approximately 2M solution. The solution was then evaporated down at 60-80°C until the resulting solid was dry, a process that took 24-72 hours depending on the metal combination being prepared. The resulting nitrate mix was then placed inside a tube furnace and heated to 750°C under a nitrogen atmosphere. After cooling, XRD was used to determine that the resulting product was in fact an oxide, and whether it was a single phase or a mix of two separate oxides. Attempts at producing a silver/copper oxide resulted in a metallic silver product, while iron/copper and nickel/copper combinations yielded a mixture of the two individual oxides. Only the iron/nickel combination resulted in a mixed metal oxide in the form of nickel ferrite.



Fig. 4. Tube furnace in use. The brown gas is nitrogen dioxide, indicating that the nitrate has decomposed.

The mixed metal powder was combined with carbon powder in a 2:1 ratio and then ball-milled overnight to ensure appropriate mixing. For each experiment 0.6 grams of the combined powder was massed and placed in a vial, then combined with 1 gram of DI water. This mixture was placed in an ultrasonic cleaner so the DI water could evenly saturate the powder. The mixture was poured into a mortar, combined with 1.57 grams of sodium hydroxide, and ground with a pestle. Based on Dr. Qiang Wang's LTE research, 1.57 grams of sodium hydroxide had been experimentally determined to yield the highest reduction efficiency.⁴ Once ground, 0.2mL Na₂S and 0.32mL H₂ suppression were added to the mortar and ground until the mixture yielded a smooth paste. Na₂S increases the electrical conductivity of the colloid by

⁴ Wang, Qiang. Personal interview. September 2016.

promoting the diffusion of O^{2-} particles.⁵ O^{2-} no longer limits the reaction rate of reduction, instead the reduction is limited by electron acceptance of the metal ions. The surface of the titanium current collector was coated with the paste, which was then covered with a polyethylene separator.

The titanium was placed in a Teflon structure and a rubber stopper was placed over the silver wire extending from the titanium disk. The structure was screwed against a second Teflon piece, holding the separator in place. The assembly was then lowered into an electrolyte bath containing the sodium hydroxide electrolyte. A piece of platinum foil attached to a silver wire extending through the lid of the Teflon apparatus was then submerged in the electrolyte bath directly above the separator, inside a hole of the Teflon structure. Each silver wire was fitted with a small piece of nickel foam and connected to a current source via alligator clamps. The apparatus was placed onto a hot plate and connected to a nitrogen source. A stir bar was placed into the electrolyte bath, and the final additives of 0.5g Na_2S and 0.3 μ L H_2 suppression were added into the electrolyte solution. The apparatus was then heated to 100°C before the current was applied via Potentiostat. Upon reaching a pre-calculated current value based on the metals undergoing reduction, the current was disconnected and the apparatus was allowed to cool to room temperature.

Once cool, the sample was removed from the titanium and placed into a centrifuge tube. The product was combined with water and run through a centrifuge to separate out the solid. This washing process was then repeated with ethanol, and the final sample was dried under a

⁵ Wang, Q., Wang, Y. *Overcoming the Limiting Step of Fe₂O₃ Reduction via in Situ Sulfide Modification*: ACS Appl. Mater. Interfaces, 2016. Print.

heat lamp. The final product was analyzed via X-Ray Diffraction to determine the composition and test whether or not the oxide had been reduced to the metallic form.

Results

X-Ray Diffraction analysis was utilized to determine the composition of the metal oxides, mixed metal oxides, pure metals, and metal alloys. XRD directs electrons at a sample, which strike and dislodge electrons in the atoms of the sample, producing X-rays. These X-rays are then detected and compared against a database containing the XRD spectra of known materials, attempting to match the sample to known compounds. XRD is most effective identifying homogeneous crystalline materials such as minerals and inorganic compounds, making it an ideal method of analysis for the samples in this experiment.⁶ The samples were prepared for XRD by first finely grinding the material into a homogeneous powder, then placing the sample on a glass slide.

XRD was utilized to confirm whether mixed metal oxides were created from their respective salts, and whether an alloy was produced from the mixed metal oxide via LTE. Attempts at producing a silver/copper oxide resulted in copper oxide and metallic silver, while iron/copper and nickel/copper combinations resulted in a mixture of the two individual oxides. The XRD spectra from these samples can be found in Appendix I. Only the iron/nickel combination resulted in a mixed metal oxide in the form of nickel ferrite.

⁶Dutrow, Barbara L., and Christine M. Clark. "X-ray Powder Diffraction (XRD)." *Techniques*. N.p., 10 Nov. 2016. Web. 8 Apr. 2017. <http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html>.

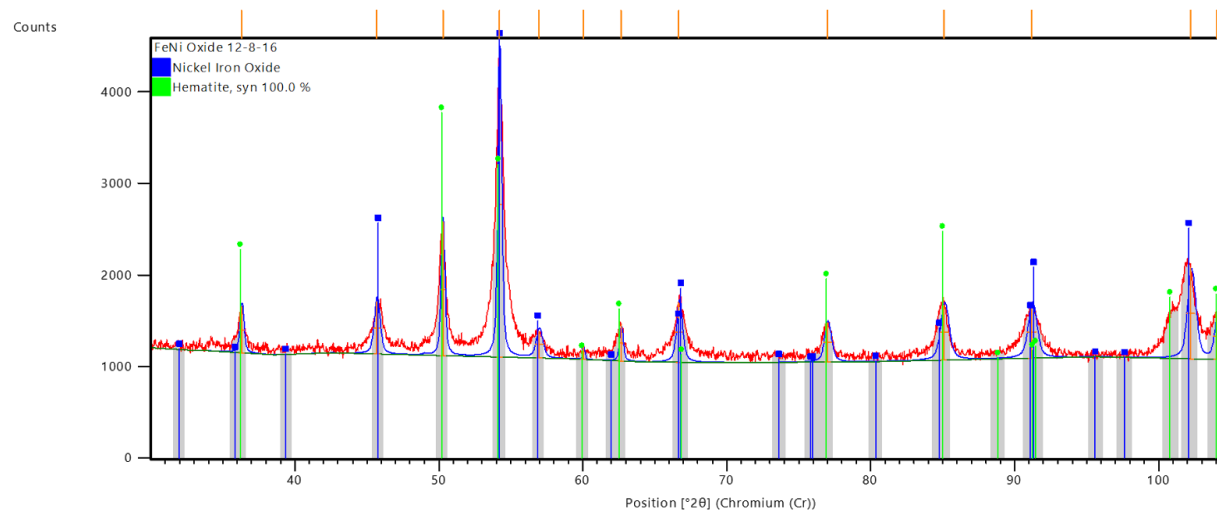


Fig. 5. XRD spectrum of first successful attempt to synthesize nickel ferrite. Seen in the sample is NiFe_2O_4 and Fe_2O_3

After successfully creating nickel ferrite, a second sample was created to ensure that it would synthesis again and to ensure there was enough mixed metal oxide to perform multiple LTE runs. This synthesis was also successful, and the XRD spectrum confirming synthesis can be found in Appendix I.

Analysis

Of all of the metal combinations tested, only the iron/nickel mixed oxide was successful, with the silver/copper, iron/copper, and copper/nickel combinations only producing a mix of the two individual oxides. The first attempt was to produce a silver/copper mixed oxide. The combination of 92.5 weight percent silver and 7.5 weight percent copper was intended to create a different method of synthesizing sterling silver. The method tested in this experiment failed because silver nitrate decomposes into metallic silver at 440°C,⁷ while silver oxide decomposes at 300°C⁸. As a result, the EDS process resulted in a mixture of metallic silver and copper oxide as depicted in the XRD spectrum found in Appendix I.

Following the failure to create a silver/copper mixed oxide, research was done on other useful metal alloy combinations. Although chromium alloys are extremely useful, forming the basis of stainless steels, the standard electric potential of chromium put it outside the group of transition metals that could be reduced (see figure 2). Further research showed that alloys of copper and nickel, known as “cupronickel” metals, have multiple marine, electrical, and coinage uses. In addition, it was theorized that the metals being adjacent on the periodic table, and therefore sharing similar properties, would mean the metal nitrates would readily form a mixed metal oxide. Unfortunately, XRD analysis of the product after calcination in the tube furnace indicated that the product was simply a combination of copper oxide and nickel oxide (see Appendix I).

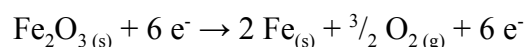
The next attempt at creating a mixed oxide, a combination of iron and copper, resulted in a similar failure. These results indicate that the procedure used is unable to synthesize a mixed

⁷ Lide, David R., ed. (2009). *CRC Handbook of Chemistry and Physics* (90th ed.). Boca Raton, Florida: CRC Press.

⁸ Lide, David R. (1998). *Handbook of Chemistry and Physics* (87 ed.). Boca Raton, FL: CRC Press. pp. 4–83.

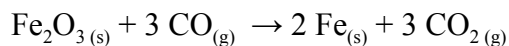
oxide with the tested combinations, and possibly that the metal chemistry for this combination simply won't allow the formation of a mixed oxide. It was only when the combination of iron and nickel nitrates was tested that EDS produced a mixed metal oxide. XRD analysis indicated that the resulting product was a combination of nickel iron oxide (NiFe_2O_4) and iron (III) oxide (Fe_2O_3). The iron oxide present in addition to the nickel iron oxide was due to high ratio of iron to nickel used when preparing the nitrate solution. The presence of pure iron oxide in the sample indicated only certain ratios of metals would form in the mixed oxide. Should the electrolysis have been successful, the ratio of metals present in the alloy would be more difficult to control than simply adjusting the ratio of nitrates during oxide creation.

The use of the mixed metal oxide for LTE was based on the success of LTE to reduce a single metal oxide. The XRD data showed that LTE of a single metal oxide successfully reduced the metal to its elemental form. The total charge input during the test was a result of the equation below, with six electrons moving from oxygen to iron per mole of iron (III) oxide being reduced. With a known amount of iron (III) oxide on the titanium electrode, the total was calculated to determine how long to run the electrolysis.

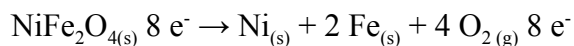


Analysis via XRD showed metallic iron mixed with carbon powder in the post electrolysis sample, confirming that the iron was reduced. The LTE process has a distinct advantage over carbothermic reduction in that the LTE procedure's only byproduct is oxygen gas, while smelting generates carbon dioxide according to the following equation. When the equations are compared, it can be seen that carbothermic reduction will generate twice the gas that LTE generates, but of greenhouse gasses instead of pure oxygen. This major difference is

also in addition to any excess carbon monoxide or other byproducts that may be generated in a blast furnace during currently used refining procedures.



While the reduction of iron (III) oxide via LTE was able to produce metallic iron, LTE of the nickel ferrite was not successful in producing a nickel/iron alloy. The procedure used for the mixed oxide was the same as that for the single metal oxide, with only slight alterations. The total charge was adjusted based on the balanced stoichiometric reduction of the nickel ferrite starting compound, which requires eight electrons to move per molecule instead of six with the iron (III) oxide, as seen in the equation below. This small increase in charge applied did not affect the voltage used, and simply required a small increase in the time the voltage was applied to the cell.



In addition to the change in charge applied, the modified mixed oxide procedure used a number of different electrolytes. Previous research by Dr. Qiang Wang had showed that metallic nickel produced side reactions and was possibly reoxidized by concentrated sodium hydroxide, like that used in the electrolyte solution. For this reason, the decision was made to use a different electrolyte for the electrolysis of the mixed nickel/iron oxide.

The first alternative to sodium hydroxide tested with the mixed oxide was sodium sulfate. A solution of 55 wt% sodium sulfate was prepared and used to fill the electrolytic cell, and the procedure was run as previously described. Unfortunately when voltage was applied to the electrodes very little current passed through the cell, resulting in an extremely low accumulation of charge. The experiment was halted after six hours, with the total charge only reaching 26

mAh. The cell was disassembled and cleaned before repeating the procedure, only to yield similar results.

Following the failure of a sodium sulfate electrolyte, LTE was attempted with a sodium perchlorate solution. As had been previously done, the old electrolyte was thoroughly cleaned from all components before the cell was filled with a 60 wt% solution of sodium perchlorate. When electrolysis was run the current was still low, but nearly double that of the sodium sulfate electrolyte. However the procedure was stopped when it was noted that an unknown white precipitate was forming in the flask used to accumulate nitrogen gas. The precipitate was collected but unable to be tested due to limited time in the lab. Research of existing literature did not show any obvious reactions between iron or nickel metals and the perchlorate ion. Future research should analyze this unknown product in order to determine the exact side reaction and how to best avoid it.

With both alternative electrolytes being unsuccessful, the decision was made to return to the sodium hydroxide electrolyte originally used for single metal oxide electrolysis. There was concern that the hydroxide could possibly reoxidize the nickel metal, however with the failure of both alternative electrolytes it was seen as one of the only options. A 60 wt% solution was prepared and electrolysis conducted on the nickel ferrite. Immediately after turning on the voltage the charge began to increase at a rate previously only seen in the single metal oxide. For this reason it is believed that sodium hydroxide plays a key role in the electrolysis. The theory is that the hydroxide ion aids the reduction/oxidation reaction by aiding the balance of charge during electron transfer. “Redox” reactions often require an acid or a base to balance the charge by converting between either OH^- or H^+ ions and H_2O molecules.

Unfortunately, as seen in the XRD data, LTE of the mixed metal oxide was unsuccessful. It is believed that there was a side reaction between the nickel metal and the sodium hydroxide electrolyte. The XRD spectrum of the post electrolysis product showed that there was a small amount of metallic iron formed. This product's formation strongly suggests that the mixed oxide was reduced, but then the nickel metal that was formed reoxidized before the XRD analysis was performed. In order for this hypothesis to be confirmed, LTE should be performed on the nickel/iron oxide using varying bases and acids. If a weaker base or an acid is able to electrolyze the nickel ferrite, then it is extremely likely that the sodium hydroxide was oxidizing the nickel. An additional option would be to use a mixed electrolyte, with a small percentage of hydroxide to enable the reaction, but the majority of the solute being a sulfate or perchlorate to prevent the electrolyte from boiling away during LTE.

Another possible cause of the unsuccessful electrolysis was the use of nickel. Although previous research by Dr. Yan Wang and Dr. Qiang Wang had indicated that nickel was theoretically within the range of transition metals that could be electrolyzed, there is a chance that nickel could not be electrolyzed on its own. This possibility could be confirmed or denied by conducting LTE with a pure nickel oxide. There is also the potential that the structure of the nickel ferrite changes the standard electric potential of the individual metal atoms. Although the individual standard potentials of iron and nickel are both below the 1.7 volts used to drive the LTE reduction, it is entirely possible that the formation of the ferrite structure changes the properties of the compound. Further testing of the mixed iron/nickel oxide must be done to determine if the standard electric potential is elevated above the potentials of iron or nickel.

Conclusions and Further Research

The results of the nickel reacting with sodium hydroxide must be confirmed through additional experimentation. It is possible that in other experiments the mixed nickel oxide will not react with the electrolyte and thus can be reduced to the alloy. Both nickel oxide and mixed metal nickel oxide should be experimented with sodium hydroxide for a full understanding of their reactivity.

Other electrolytes besides sodium hydroxide should be tested to determine their effectiveness in LTE. Sufficient data with a wide range of electrolyte solutions could be used to determine the electrolyte capable of greatest reduction efficiency. Additionally, the concentrations of these electrolytes in solution should be varied to determine the effect of concentration on reduction. Data for multiple electrolytes as well as mixed oxide experiments should be compiled for future applications.

References

Dutrow, Barbara L., and Christine M. Clark. "X-ray Powder Diffraction (XRD)." *Techniques*. N.p., 10 Nov. 2016. Web. 8 Apr. 2017.

Lide, David R. (1998). *Handbook of Chemistry and Physics* (87 ed.). Boca Raton, FL: CRC Press. pp. 4–83.

Lide, David R., ed. (2009). *CRC Handbook of Chemistry and Physics* (90th ed.). Boca Raton, Florida: CRC Press.

<http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html>.

Redkin, A., Apisarov, A., Dedyukhin, A., Kovrov, V., Zaikov, Y., Tkacheva, O., Hryn, J. *Recent Developments in Low-Temperature Electrolysis of Aluminum*: ECS Transactions, 2012. Print.

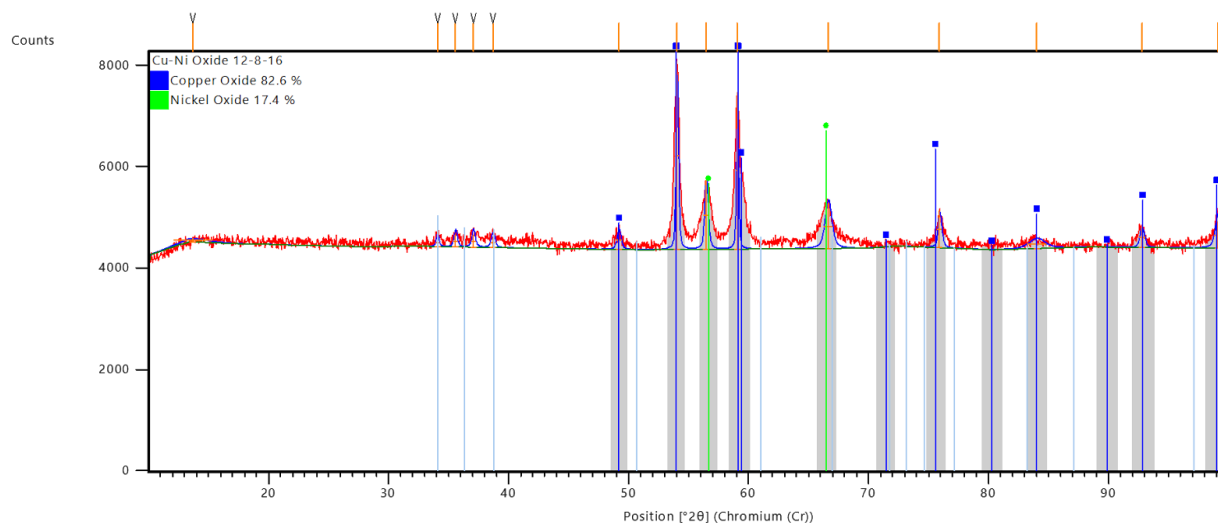
Rossetti, G., Burger, J., Sisson, R. *Characterization of Mixed Cobalt-Molybdenum Oxides Prepared by Evaporative Decomposition of Solutions*: J. Am. Ceram. Soc., 1989. Print.

Wang, Qiang. Personal interview. September 2016.

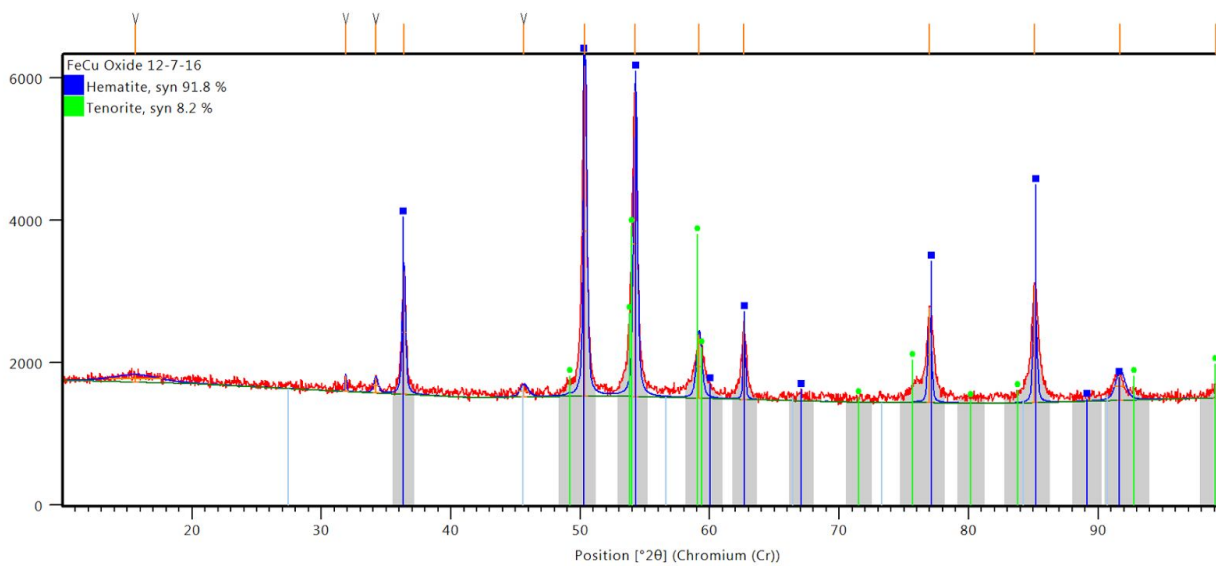
Wang, Q., Zhu, Y., Qiuyang, W., Gratz, E., Wang, Y. *Low temperature electrolysis for iron production via conductive colloidal electrodeI*: RCS Advances, 2014. Print.

Wang, Q., Wang, Y. *Overcoming the Limiting Step of Fe₂O₃ Reduction via in Situ Sulfide Modification*: ACS Appl. Mater. Interfaces, 2016. Print.

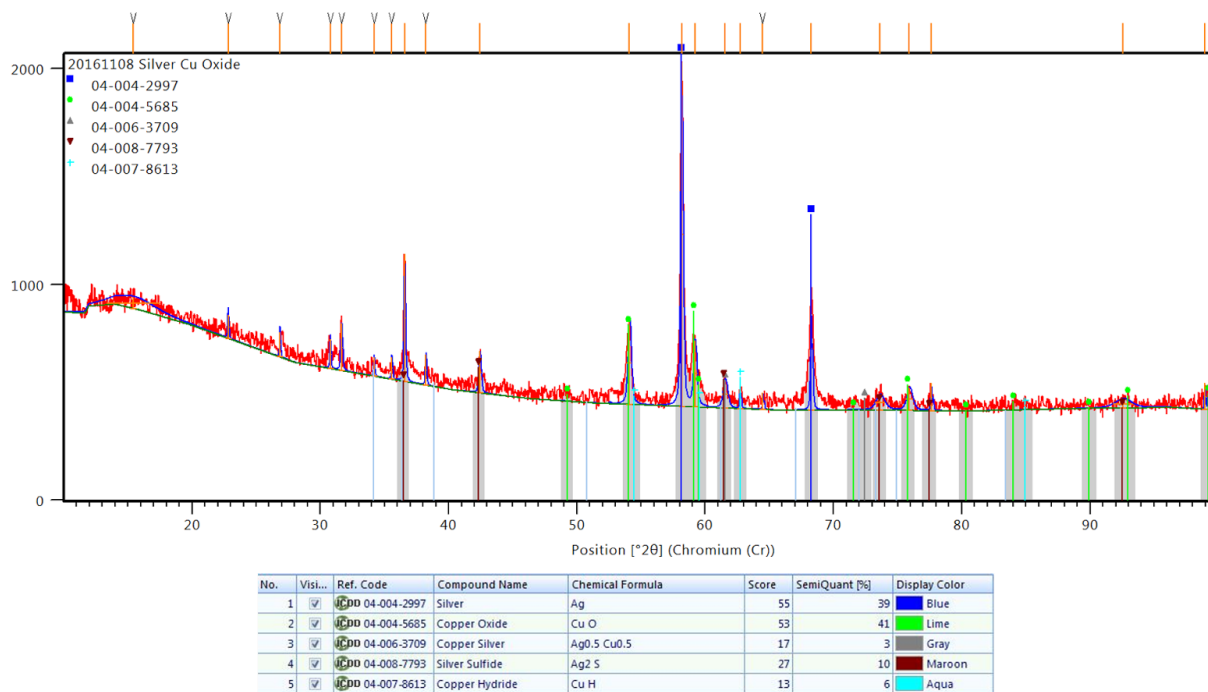
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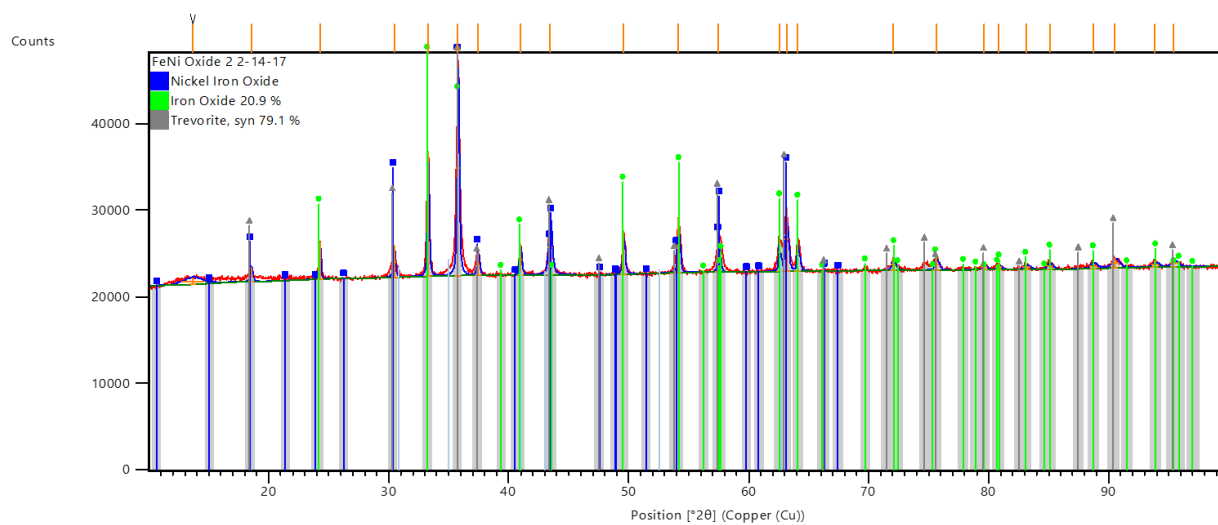
This XRD spectrum shows that the attempt to create a nickel/copper oxide was unsuccessful, creating separate CuO and NiO.



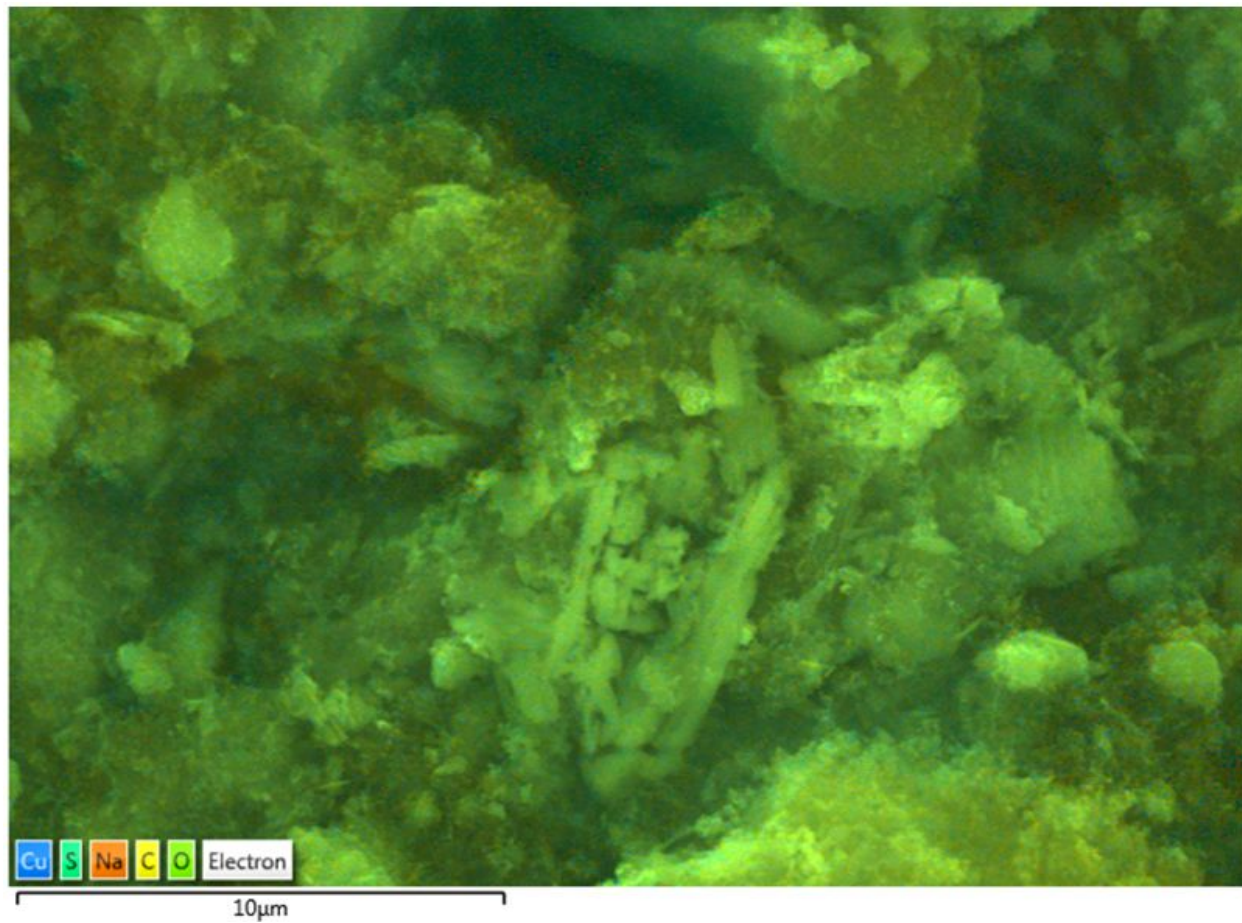
This XRD spectrum shows the unsuccessful attempt to create an iron/copper oxide, resulting in hematite (Fe_2O_3) and tenorite (CuO).



This XRD spectrum shows the result of attempted synthesis of silver/copper oxide, creating metallic silver instead of silver oxide.



This XRD spectrum is from the second successful attempt to create Nickel Iron Oxide; the two compounds found in this sample are trevorite ($\text{NiFe}^{3+}_2\text{O}_4$) and iron oxide.



SEM Layered Image of a post electrolysis sample of nickel ferrite.