Recycling of ECM Metal Hydroxide

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The electro chemical machining (ECM) process is one that dissolves metal into a hydroxide form as metal is removed from a part. There is approximately 10 kg of hydroxide formed for every 1 kg of metal removed. Over 1500 tons of hydroxide is produced at Sermatech-Lehr each year. The hydroxide may contain Hexavalent chrome in the electrolyte solution mixed with the hydroxide. For this reason, 100% of the hydroxide is currently recycled so there is no landfill or other disposal concerns. This paper will discuss the process from the generation of the hydroxide through the entire process resulting in metallic metals being made from the hydroxide. Terry Lievestro from Sermatech follows the process up to the point the material is picked up by Agmet metals inc. John Rankin from Agmet Metals Inc. provides the information for the rest of the process.

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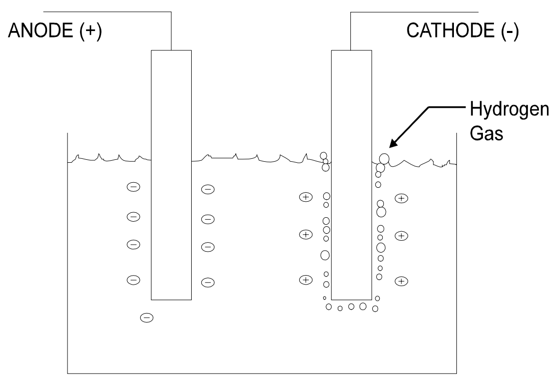
1.0 How is ECM Metal Hydroxide Created?

Electro Chemical Machining (ECM) works on the principle of the simple electrolytic cell we all learned in high school chemistry. In the simple cell (Fig. 1.1) two electrodes are placed in a conductive solution. In the case of ECM, we use a saltwater solution such as everyday table salt (NaCl). A DC potential is applied between the electrodes. The positive electrode is referred to as the anode and the negative one as the cathode. Because there is an electrical potential between the electrodes, current will flow between them. Bubbles of hydrogen gas (H_2) can be seen bubbling up from the cathode. The anode will begin to "corrode" as the electrons flow from it toward the cathode. As equation 1.1 below shows, the water (H_2O) is broken down with the electron flow resulting in H_2 gas and hydroxide ions (OH-).

Figure 1.1 – Simple Electrolytic Cell



Ions = electrically charged groups of atoms.

(eq. 1.1) $2H_2O + 2_e- \Rightarrow H_2 + 2OH^-$
Transfer of electrons between ions and electrodes

(eq. 1.2) $Fe \Rightarrow Fe^{2+} + 2_e-$

(eq. 1.3) $Fe^{2+} + 2_e- + 2H_2O \Rightarrow Fe(OH)_2 + H_2$
Metal Hydroxide + gas

As the electrons flow from the anode (in this case made from iron [Fe]), equation 1.2 shows the Fe^{2+} ions are released from the anode. When we put the reactions together in equation 1.3, we see the Fe^{2+} ions bonds with the OH- hydroxide ions. The result of this is the formation of iron hydroxide and hydrogen gas.

The result of increased current flow is an increase in the material removal rate. The part to be machined by ECM is made the anode. The tool to generate a shape is made the cathode. A near mirror image of the desired shape is cut into the cathode. With voltages in the 10 to 25 volt ranges and amperages of up to 40,000 amps mean it is not uncommon for 1000 KW of power to be consumed. Different electrolyte salts are used for different applications. Sodium Chloride (NaCl) is the most common salt used. This is an inexpensive general-purpose electrolyte that is easy to store, handle and control. Sodium Nitrate ($NaNO^3$) is another common one. Other salts have other advantages for specific alloys that are beyond the scope of this paper. The thing to point out here, though, is most ECM applications use a water-based electrolyte. The pH levels are normally maintained in a neutral state so an operator can work with the electrolyte easily. There are forms of ECM that use an acid based electrolyte. These are usually used to generate small holes and the process is sometimes referred to as "Stem Drilling". This paper does not include this sub category of ECM.

SUMMARY OF ECM FUNDAMENTALS

- The part or work piece is charged positive (+).
- The tool or cathode is charged negative (-). It is given a inverse of the shape to be formed.
- A water and salt-based electrolyte is circulated between the cathode and the part at pressures of 7 to 24 bar (100 to 350 psi).
- 10 to 25 volts DC are applied from a 5,000 to 40,000 amp DC rectifier.
- Positive ions of metal leave the part surface and most become particulates in the electrolyte.
- Hydrogen gas forms on the tool surfaces and is removed with a ventilation system after electrolyte flushes it from the cut.
- Metal ions and hydroxide ions join to form metal hydroxide.
- Gas and metal hydroxides are washed from the gap and returned to the electrolyte tank.

2.0 Are there Environmental concerns?

ECM does produce Hexavalent Chrome along with Trivalent Chrome. The trivalent chrome is a precipitate that can be filtered out of the electrolyte. The Hexavalent chrome and other "heavy metals" are in solution and cannot be filtered out. These present a problem to the environment if they get into the ground water. All facilities that have the ECM process must then have a containment system to ensure no environmental damage. Electrolyte systems are typically a closed loop system where electrolyte is filtered and reused. The resultant hydroxide must then be recycled as described in this paper.

In the closed loop electrolyte system, Hexavalent chrome will build to a saturation level of approximately 3,000 ppm. After this point, it tends to convert to Trivalent chrome. The hydroxide is in a filter cake form when it is shipped to recycling. There is a certain amount of Hexavalent chrome in the liquid portion of the filter cakes. This is also recycled as the water is burned off during the recycling process.

Because of the hydrogen formed in the ECM process, a ventilation system is used. Each ECM machine has enough air forced through the enclosure to ensure hydrogen does not build up to dangerous levels. The machines can continue to operate as long as enough airflow is passing through the exhaust duct. All the machines are connected to a central ventilation system. This system uses a double scrub system to remove all water droplets from the air being discharged into the atmosphere. The water used in the washing of the air is then discharged into the "wash water system" which is discussed later. The chrome and other metals are all removed and sent to recycling.

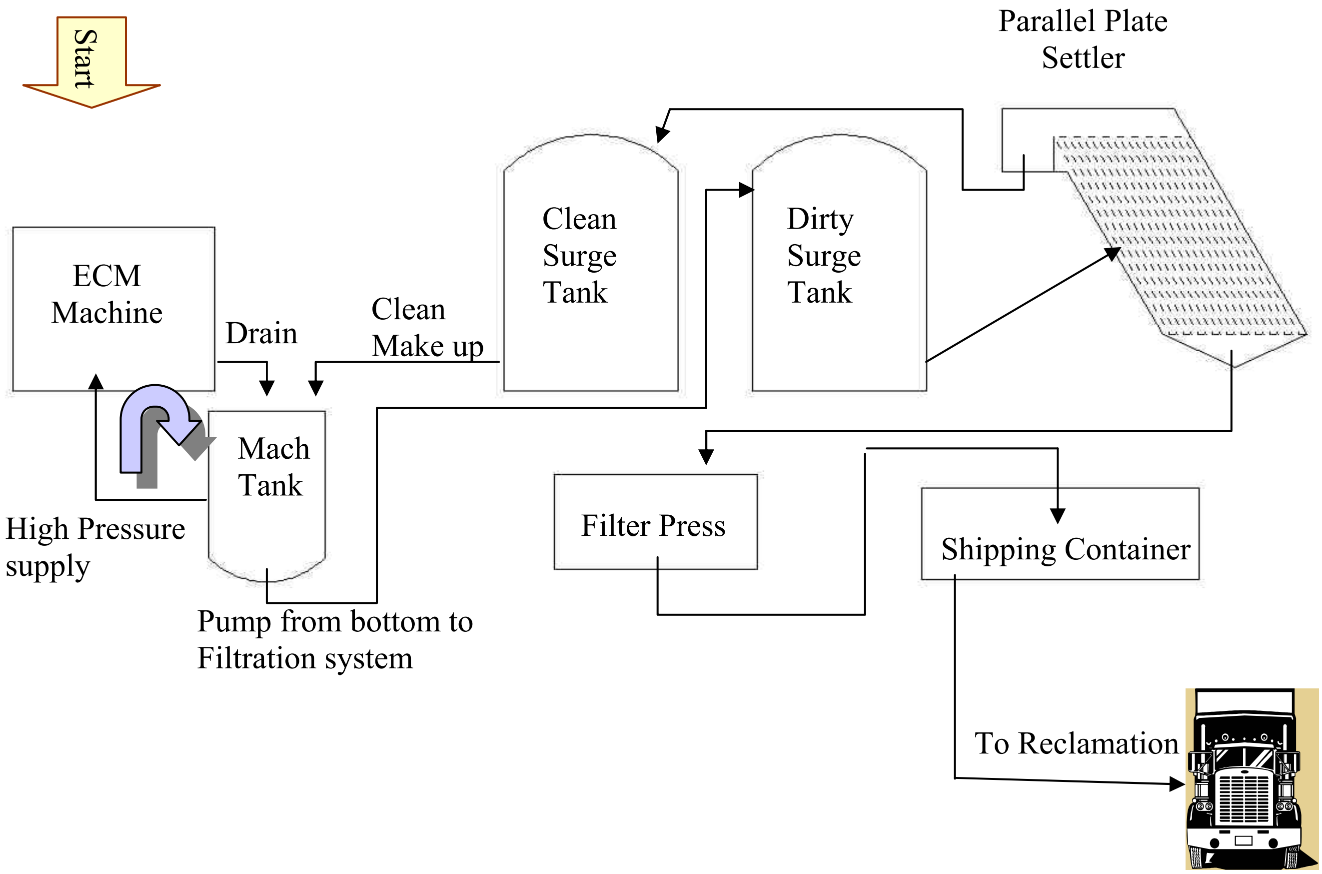
All parts machined by ECM will have a film of electrolyte on them. As a result, they are rinsed to remove all traces of electrolyte. Floors are washed and all other items with electrolyte on them are all cleaned to remove electrolyte traces. All this water is discharged in a wash water system. All floor drains and any drain in the ECM areas are all connected to the wash water system. Only the restrooms are connected to the sanitary sewer system.

All buildings are designed such that any spill or leak is captured by the wash water system. Different floor levels, pits, curbs, and ramps are methods used to ensure the spills are captured. All these waters flow by gravity to a low point in the building where it is then pumped to the wash water system for treatment. All activities associated with the entire ECM area must be in compliance with the Federal Environmental Protection Agency, the Sate of Ohio, the City of Blue Ash, and the Metropolitan Sewer District.

3.0 Hydroxide Closed Loop System

The Hydroxide is created in the ECM process at the ECM machine. Figure 3.1 below is a schematic diagram of the closed loop system. This is also known as the electrolyte system. Each facility has multiple parallel electrolyte systems for various different electrolytes such as sodium chloride or sodium nitrate. All electrolytes systems however discharge filter cake into the same shipping container.

Figure 3.1 – Hydroxide Closed Loop System



In the ECM Machine, the part is mounted on a fixture that locates it and passes power into it. The cathode, or cutting tool, is mounted on a manifold that passes electrolyte across the cut gap. The machine then has a gravity drain to a holding tank. Figure 3.2 shows the machine with a part and cathode. The colors are a result of the hydroxides and Hexavalent Chrome. Figure 3.3 shows the drain and high-pressure piping to the machine from the electrolyte system. For every kilogram of metal removed by ECM, approximately 10 kilograms of hydroxide is created.

Figure 3.2 – ECM Machine

Figure 3.3 – Machine Piping

Figure 3.4 – Electrolyte Holding Tank

The holding tank has multiple purposes in the ECM system. It is a dish bottom tank that has a drain on the bottom. It is also the vessel used to feed the high-pressure electrolyte pump that supplies the ECM cathode with electrolyte. A heat exchanger system is also attached to the tank to maintain the temperature of the electrolyte in the process. A float valve system in the top of the tank maintains the tank at a constant volume as heavier hydroxides are drained from the bottom. In most instances, the tank is replenished with clean electrolyte every four hours. This level of recirculation keeps the solids content of the electrolyte at an acceptable level for most processes. In some applications, extremely clean electrolyte is required. For these applications, no holding tank is used at the machine. The electrolyte is provided to the machine from the electrolyte filtrations system directly to the machine. This type of system requires a significantly larger filtrations system as described below.

The dirty electrolyte from the ECM machine passes through its holding tank through the dish bottom to a surge tank in the filtration area. From here it is pumped in a controlled basis to a parallel plate settler or clarifier. These clarifiers are usually having the plates on a fifty-five degree angle. The electrolyte is mixed with a flocculent in a pre-mixer as seen in figure 3.5. It is then passed from the lower section of the plates and up over a weir as seen in figure 3.6. The electrolyte entering the clarifier is at approximately 3,000 ppm coming from the machine holding tanks. Approximately 90% of the electrolyte passes over the weir and is sent to a supply tank that feeds the machine holding tanks with clean electrolyte. The remaining electrolyte is then removed from the bottom of the clarifier in a thickened state of approximately 30,000 ppm.

Figure 3.5 Clarifier Top View

Figure 3.6 Clarifier Close View

The flow from the top of the weir is pumped to the supply tank as described above. This supply tank is then piped to the ECM machine holding tanks. In each machine tank, a float system is used to add clean electrolyte to the tank to maintain the level. Each ECM machine tank may be supplied by different electrolytes. Each electrolyte system has a similar supply and drain system at each machine. The electrolyte system operator can drain each machine holding tank and flush it. They then reconfigure the valves such that a different electrolyte can be added to the tank and drained to the appropriate system.

The drain from the bottom of the clarifier is pumped to a surge tank. A diaphragm pump is then used to pump this thickened dirty electrolyte into a filter press. The filter press is a device with a stack of hollowed out plates with a durable filter cloth. The dirty electrolyte is pumped into the cavities formed by adjoining plates. The flow must pass through the filter cloth to exit. The cloth is rated a 3 to 5 micron filter. The filtered electrolyte is returned to the clarifier surge tank where it is passed into the cycle again in case solids may have escaped with the electrolyte. The solids filtered by the cloth continue to build up until the cavity is full. As the cavity fills, the flow rate through the press drops. When the flow rate drops to a predetermined level. The feed pump is shut down and air is injected to further dry the cake formed between the plates.

Figure 3.7 – Stand Alone Filter Press

Figure 3.8 – Filter presses with Conveyor

Figure 3.7 above a filter press is shown with catch bins below. Figure 3.8 shows multiple filter presses above a conveyor system. For systems generating a lot of filter cake it would be best suited to have the conveyor system. For smaller systems that don't generate a lot of cake, these systems may get by using the bins that can then be dumped into a transportation container. Figure 3.9 below shows a conveyor system capable of loading a drop box, shown in figure 3.10, evenly over the length. Approximately 20 tons of filter cake can be loaded into each drop box.

Figure 3.9 – Filter cake Conveyor

Figure 3.10 – Transportation Drop box

Each of the transportation drop boxes has a heavy plastic liner. The liners are used in addition to the door seals to ensure no leakage during transit. A truck, shown in figure 3.11, is used to pull the drop boxes onto itself for transportation. An empty is then placed ready to load again. In the system shown in figures 3.9 and 3.10, two-drop boxes can be filled with the same conveyor. When a drop box is filled, the Recycler sends his truck to come pick up the full drop box and leave an empty. The Recycler pays for the value of the recycled material in the filter cake. A later section will describe the handling of the material after is transported.

Figure 3.11 – Drop box Truck

4.0 Facilities Containment

No discussion of recycling hydroxide would be complete without discussing the containment necessary to prevent environmental hazards. Being a responsible company requires more than just sending the material to recycling. The entire facility must be designed and maintained to prevent damaging the environment with the heavy metals and other contaminants associated with the ECM process. With a proper system, the risk of harm can be reduced to nearly zero.

Figure 4.1 – Liner installation

Figure 4.2 – Completed Liner

The facility must be built with the assumption that there will be a spill or leak at some time. Every effort may be made to prevent this, but the fact that it is always possible for an accident to occur, means preventive measures require proper containment. Buildings where ECM is used are best if built on top of a rubber liner. Figure 4.1 shows workers vulcanizing sheets of rubber to form a watertight liner before concrete is poured. Figure 4.2 shows a trench that will have a drain put on top of the liner. All drain lines must be above the liners in the event that they leak at some future date.

Figure 4.3 – Liner on walls

Figure 4.4 – Liner under Footer

Figure 4.5 – Drain on top of Liner

Figure 4.6 – Drain Sump Tank

Figure 4.4 shows that even the footers are built on top of the rubber liner. In figure 4.3 it is clear that the rubber is brought above all foundation walls. Figure 4.5 shows a drain trough being placed on top of the rubber liner. The drain leads to a sump that is a double walled tank with a pump. Gravity is always used to bring the spills and leaks to the sump. In the event of a power failure, the sumps are always in a pit area below the shop floor level. The volumes these pit areas can hold are always greater than the volume of electrolyte in this area of the facility. The floors are also sealed with epoxy. All corners and expansion slots are filled with sealers and then a grouted epoxy is used to further ensure no leakage. Alarms are used to indicate the sump has over filled so action can be taken immediately.

In addition to keeping all drains above the liner, all pressurized lines are kept above the floors. Service tunnels are used to connect buildings and other areas where is undesirable to have piping overhead. In this way, if a pipe were to develop a leak, it would leak out onto the floor of the tunnel where it is visible and alarms are used to notify system operators. No pressure is then forcing electrolyte under the floor to be contained by the liner. Figures 4.7 and 4.8 show service tunnels used to run pressurized pipes.

Figure 4.7 – Service Tunnel

Figure 4.8 – Service Tunnel

Figure 4.9 – Filtration Mezzanine

Figure 4.10 – Pit area with Tanks

In the Filtration Systems area where multiple large volume tanks are used, pit areas are used for secondary containment. Where in the past, settling pools were used by many in the ECM business instead of the more expensive clarifiers, now pools are used to hold tanks. Now buildings are built with the entire filtration area in a pit area where gravity is used to flow everything down to the filtration area. Figure 4.9 shows a facility where equipment is placed on top of mezzanines built over the pit area where tanks are placed. Figure 4.10 is taken from the bottom of the pit area showing tanks and pumps. This type of system is very good at maintaining secondary containment for the large volumes of electrolyte.

Figure 4.11 – Wash Water Treatment System

Mentioned numerous times before, a wash water system is used to capture and treat all water that may have been contaminated. The wash water system has numerous tanks to hold the water that is pumped from the drain systems through out the facility. When a tank is full, the water is then pumped into another tank while the first tank is being treated and released. A very stringent procedure is used to treat and release water to the sanitary sewer system.

After the tank is full, an operator will start a process that involves pumping Sulfuric Acid into the holding tank to bring the pH to approximately 2.0. A mixer is used, as is a recirculating pump, to ensure proper mixing. After the proper pH is achieved, Sodium Bisulfite is then added to the system. This will reduce the Hexavalent chrome to Trivalent Chrome, which is a precipitant. Other heavy metals will also be reduced during the process. The water will be tested until no Hexavalent Chrome can be detected. Sodium Hydroxide is then pumped into the tank to bring the solution back to a neutral state of about pH 7 to 9.

After the tank is free of Hexavalent Chrome, it is then pumped through a filter press to remove all solids. The solids from this press are shipped with the filter cakes from the filtration of electrolyte for recycling. This closes the loop and results in all dissolved metal being sent for recycling.

When the tank is free from all solids, the metropolitan sewer district is called. They have the option of coming to sample the water before it is released or to authorize it being released. They also have a sampling well outside of the facility in which they can come at any time to test water that has been released.

Figure 4.12 Ventilation Scrubber

The air drawn from all ECM machines and tanks is cleaned before releasing it to the atmosphere. Because hydrogen is given off in the ECM process, all machines and tanks are connected to a ventilation system to remove hydrogen gas. The level of hydrogen is minimal with a flow of air through the enclosures. The ventilation system has a duel stage scrubber to ensure no droplets of electrolyte are released to the atmosphere in this ventilation air. The water from the scrubber is then cycled through the wash water system for cleaning.

5.0 Filter Cake Elements

The value of the filter cake for the Recycler is based on the elements in the filter cakes. The exact composition varies based on the type of metal being machined. If there is no chrome in the alloy being machined, then there is no chrome in the filter cakes. The salt in the cake is a factor of which electrolyte is being used to machine with ECM. This may be sodium chloride or sodium nitrate. The one constant in a filter cake is the fact that nearly 75% of the filter cake by weight is water. A filter press is limited in its ability to remove water. It becomes impractical to mechanically remove water. The recycler uses a thermal process to be defined later.

Figure 5.1 – Filter Cake Element

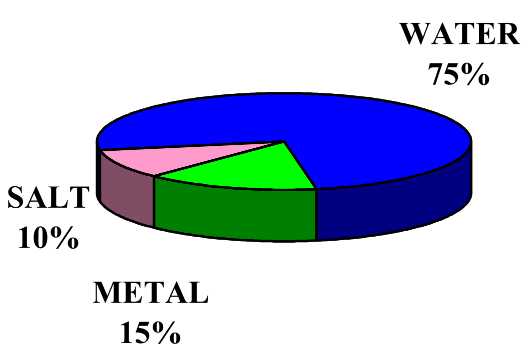
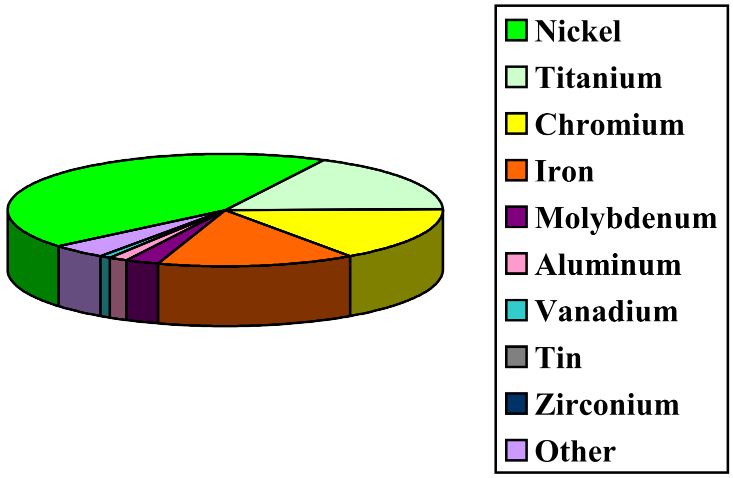


Figure 5.2 – Metal Breakdown of ECM Filter Cake



For most situations an ECM filter cake will contain approximately 75% water, 10% salt, and 15% metal by weight. For the majority of the filter cake processed from our facility, Figure 5.2 shows a typical breakdown of the metal. You will see the largest constituent is Nickel. This is a result of the fact that the Jet Engine Industry is one of the largest users of ECM because of the difficulty in conventional machining of their alloys. Other industries such as the medical industry use a lot of Cobalt and Chromium. These are also difficult alloys to machine and may use ECM as an alternative to conventional machining. Furthermore, titanium is used by both of these industries along with other ones like the golf industry for drivers. From Figure 5.2 you will see ECM also machines a lot of titanium for the same reasons just mentioned. The metals from the filter cake end up as alloying input for the primary metal industry as described in the next section.

6.0 Processing of the Filter Cake back to Metal

The Recycler picks up the drop box shipping containers, as described in section 3.0, and brings them to his Oakwood Village, Ohio facility seen in Figure 6.1. The ECM filter cake is off loaded into a bulk storage building, which was originally designed to handle hazardous wastes. This facility takes materials in many different forms. Some materials are received in tanker trucks as seen in the foreground of Figure 6.1. Materials requiring drying are processed through a refractory lined ten-foot diameter by one hundred ten foot long natural gas fired calciner.

In the bulk storage building, the ECM filter cake is then sampled for the metal content. It is then blended with other materials of varying metal content prior to processing. The blended material is then stored in the building until ready for processing through the calciner. Figure 6.2 shows a sample of different blends waiting for processing.

Figure 6.1 - Recycler Facilities

Figure 6.2 – Bulk Storage Building

To dry the blended materials, they are fed into a gas fired rotary calciner shown in Figure 6.3. The materials are subjected to high temperatures to drive off moisture. The result is that all organics and moisture are volatized leaving a metal oxide ash. For example $Fe(OH)_2$ is converted to $FeO + H_2O$ and the H_2O is then evaporated off. The process gases are passed through an afterburner; quench tower, and bag house before leaving the stack as clean steam.

Figure 6.3 Rotary Calciner

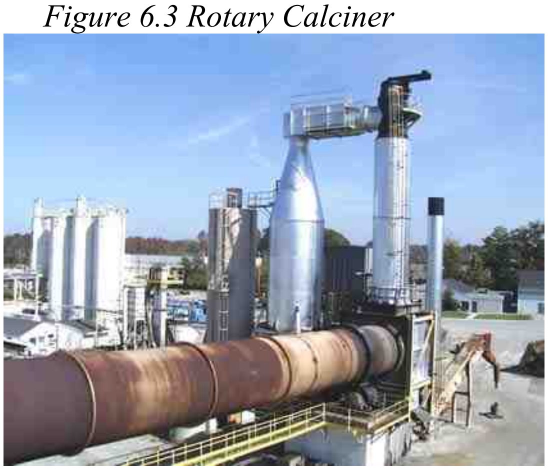


Figure 6.4 Emission Stack

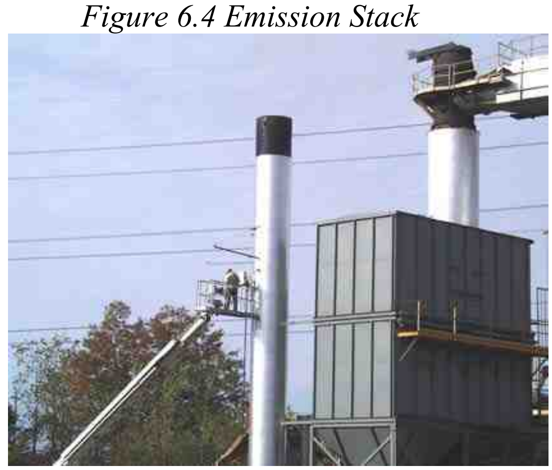


Figure 6.5 – Bag House

The bag house (Figure 6.5) consists of two chambers housing two hundred eighty eight bags each. Particulate captured in the bag house is commingled with product exiting the calciner. The calcined product is conveyed through enclosed screw conveyors in order to contain dust. The product is de-dusted, packaged, and analyzed prior to shipment to the smelter. The exhaust stack seen in Figure 6.4, is tested annually for particulate emissions. These tests have consistently demonstrated the ability to operate at less than 50%of the permitted emissions limitations.

After the material is calcined at the Recycler, he ships it to a primary metal company in Super Sacks. The primary metal company may vary by composition of the calcined material. The metal oxide ash is used as smelter feed at the primary metal manufacturer. At the converter, molten ore is purified by the removal of slag. Figure 6.6 shows the smelting process. Final purification of the individual metals occurs at the refinery. Metal anodes are electrochemically dissolved and selectively deposited onto the cathode resulting in 100% reclamation of the ECM filter cake.

Figure 6.6 – Smelting Process

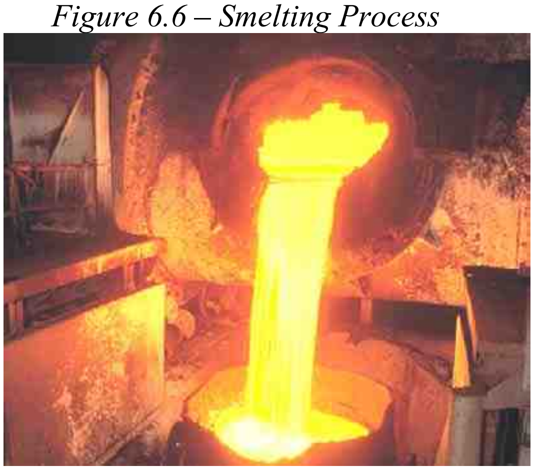
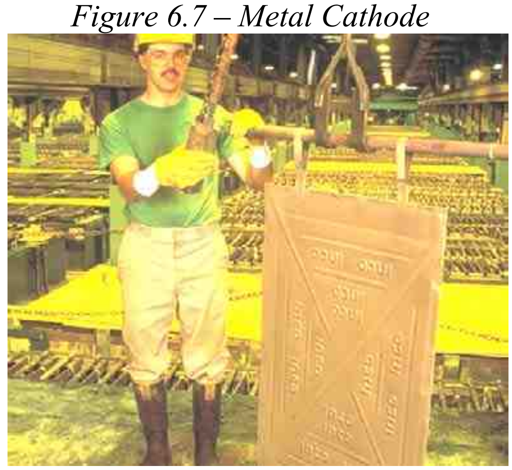


Figure 7.7 – Metal Cathode



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