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AN IMPROVED PLATING PROCESS

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ABSTRACT

An alternative to the immersion process for the electrodeposition of chromium from aqueous solutions on the inside diameter (ID) of long tubes is described. The Vessel Plating Process eliminates the need for deep processing tanks, large volumes of solutions, and associated safety and environmental concerns. Vessel Plating allows the process to be monitored and controlled by computer thus increasing reliability, flexibility and quality. Elimination of the trivalent chromium accumulation normally associated with ID plating is intrinsic to the Vessel Plating Process. The construction and operation of a prototype Vessel Plating Facility with emphasis on materials of construction, engineered and operational safety and a unique system for rinse water recovery are described.

HISTORY

Development of high performance ammunition for heavy artillery following the second world war presented new and challenging problems to the gun designer. Higher velocity, temperature and pressure caused gun tubes to erode at a much faster rate than had been previously experienced, resulting in reduced service life for the gun tube. Electrodeposition of chromium to the bore of small caliber tubes had resulted in enhanced bore life, consequently the decision was made to test chromium plate in large caliber tubes as an erosion barrier.[1]

Electrodeposition of chromium had been accomplished in immersion processes requiring tanks large enough to completely immerse the part to be plated in the various cleaning, rinsing, pre-treatment and plating solutions. Lacking facilities to immerse a gun tube as long as twenty-five feet, researchers in Great Britain developed two alternative processes, one requiring only partial immersion and one requiring no immersion. The partial immersion process, and no immersion process to a lesser extent, were developed to apply conventional high contraction (HC) chromium to the bore of long gun tubes. A number of tubes were plated with favorable results.[2]

Early work in non-immersion plating demonstrated the advantages of chromium plating but was replaced with the more conventional immersion plating processes for a variety of reasons. The quest for higher performance artillery and tank cannon however has not been replaced but instead has brought us to the point where conventional HC chromium is only marginally acceptable as a bore coating. An alternative form of chromium has shown promise as a more protective bore coating, however the conditions required to deposit this coating preclude the use of immersion plating. A non-immersion or vessel plating process (VPP) was developed to evaluate this coating in full size large caliber gun tubes. This VPP draws heavily on previous work with significant enhancements in process control and pays particular attention to hazardous waste reduction.

Low contraction (LC) chromium, as opposed to conventional (HC) chromium, retains the body centered cubic crystal formation but exhibits a difference in grain growth pattern as well as a lack of the micro-crack network prevalent in HC chromium. Deposition of LC chromium is achieved at elevated solution temperatures and high current densities. These two requirements cause excessive solution loss, through evaporation, and gas generation when used in an immersion system. Tremendous amounts of energy are required to maintain immersion tanks of the required size at process temperature, thereby increasing the cost of the plating operation. Maintaining tank integrity for prolonged periods at operating temperature has also proven to be a problem. These difficulties could be overcome with proper system design and material selection, however the high current densities required and the large volume of gas generated at the anode and cathode present a problem which cannot be adequately addressed in the immersion process.

Hydrogen gas is generated at the cathode and oxygen gas at the anode during electrodeposition of chromium. Plating of internal diameters will only allow these gases to rise through the annulus. Since the gases are generated along the entire length of both the anode and the cathode they accumulate as they rise, increasing the ratio of gas to liquid along the length of the tube. Resistance of the plating solution increases with the increase in gas to liquid ratio causing a reduction in the plating rate. The result is a tube with a heavy coating at the lower end and a thin coating at the upper end.[3] In the extreme case no chromium is deposited at the upper end. This phenomenon occurs during deposition of HC chromium and is addressed thorough anode design, however at the current densities required to deposit LC chromium anode modification is not effective in reducing the tapering effect. Increasing the flow rate of plating solution through the annulus has been shown to reduce the tapering effect.[3] This is accomplished quite easily in the VPP. Higher flow rates have the added benefit of higher plating rates and thermal stabilization of the system. A comparison of the two plating processes can be seen in Fig. #1.

DESIGN PARAMETERS

Development of the VPP was a step toward the larger objective of evaluating LC chromium in a variety of large caliber artillery and tank cannon, consequently the design parameters for a prototype facility were well defined. The vessel plating facility (VPF) is described here as two major systems, the control system and the plumbing system. The plumbing system is further divided into two subsystems: facility and process plumbing.

The process control system was designed to perform the following tasks:

- i monitor record and control valve and pump sequences
- ii monitor record and control rectifier function
- iii monitor record and control flow rates and pump pressure
- iv monitor record and control tank temperatures, fluid levels and chemical concentration
- v monitor and record chromium thickness[4]

These control functions, with the exception of item v were accomplished with off the shelf sensors and Allen-Bradley 2/30 PLC.

The facility plumbing subsystem consists of the steam and water supply for cooling and heating process solutions, rectifier cooling and pump seal water. The piping, valves and pumps which move process solutions though the gun tube and back to the proper tank constitute the process plumbing subsystem.

MATERIALS AND CONSTRUCTION

Material selection for facility plumbing was straightforward due to the standards for handling steam and water, however materials selected for the process plumbing subsystem required resistance to concentrated sodium hydroxide, concentrated acids as well as temperatures approaching 200 F at relatively high flow rates. Gaskets and seals required the same properties in addition to providing electrical isolation in some cases. Materials for the facility were selected considering these requirements and the anticipated operation schedule.

Figure 2 is an artist's representation of the Vessel Plating Facility. Although incomplete (all hardware not shown) it does provide a basic description of the pump-through concept.

Process tanks are 1200 and 600 gallons for chromium plating and pre-treating solutions respectively. All process tanks are lead lined steel. Heating and cooling capacity is provided with carbon filled teflon thin tube heat exchangers. Hypalon gaskets are used to seal CPVC pipe flanges connecting each tank to its respective pump. The pair of Kynar lined pumps on the chromium side are plumbed such that either pump can be fed from either tank. This increases reliability of the system and allows for the pumps to be run in tandem. Pumps servicing the caustic cleaner and electropolish tanks (not shown) are also plumbed for dual service although tandem pumping is not desirable. CPVC was selected for this application due to its excellent resistance to all chemicals involved even though the recommended temperature range was marginal. CPVC is also used between the caustic and electropolish pump outlets and the main vertical stack, the main vertical stack, and all return lines for caustic and electropolish solutions as well as parts of the chromium solution return line.

Pressures and temperatures between the chromium pump outlets and the main vertical stack are somewhat higher than the pre-treatment side. Safety and reliability precluded the use of CPVC for this application. A Kynar lined, fiberglass filled, phenolic resin pipe was specified. This pipe provides excellent chemical resistance and the additional strength needed here for safety and reliability. Phenolic resin overap reduced the concern of chemical attack from the pipe outside diameter (OD) which would have been a problem with Teflon lined steel pipe in a location where any of the solutions could drip on the pipe.

The main vertical stack terminates at the bottom builder (not shown) which is the steel structure that supports the weight of the gun tube and the anode. A combination of UHMW polyethylene, teflon and silicone seals are used here for reliable joining of the gun tube to the process plumbing and electrical isolation. These seals also serve to locate the gun tube and the anode on the same axis which is critical for concentric chromium deposition.

The "birdbath" is a four outlet manifold located on top of the gun tube. Here again a combination of seal materials are used for reliable joining and insulation. In addition to directing fluid flow this fixture locates the anode on the gun tube axis and provides two safety features. A rupture disk plumbed to a pressure relief valve is connected to one of the manifold outlets. This safety device is designed to release excess pressure generated by rapid expansion of hydrogen gas which can accumulated in the system. A second manifold outlet is fitted with a vacuum relief valve for relief of vacuum created by pumping large volumes of fluid through a closed system. At pump shutdown this vacuum can exceed 80 psi resulting in damage to process plumbing. As previously mentioned the plumbing from the birdbath back to the caustic and electropolish tanks is CPVC. Teflon lined steel pipe is used to return chromium plating solution to a level below the main deck. High flow rates and safety concerns preclude the use of CPVC for this pipe run. A leg off the chromium return line goes to a 300 gallon lead lined holding tank (not shown) which will be discussed later in this paper.

Electrically actuated CPVC ball valves are used in most 4" and all 2" applications. Teflon lined electrically actuated butterfly valves are used in the chromium pump supply plumbing as well as the main vertical stack for their compact size and better reliability over large temperature spans.

Process plumbing is the most critical subsystem in the Vessel Plating Facility, determining to a large extent the reliability and versatility of the Facility. This design has provided many hours of reliable operation with enough versatility to support development of production processes as well as investigations into many phenomenon unique to vessel plating.

PROCESS CONTROL

Electrodeposition of chromium in the Vessel Plating Facility consist of four steps, caustic cleaning, electropolishing, reverse etching and chromium plating. Each of these steps is followed by a water rinse. Valve and pump actuation, rectifier control, as well as process solution temperature and level control are accomplished by the process control subsystem.

An array of sensors and test instruments feed an Allen Bradley 2/30 Programmable Logic Controller (PLC) with information needed to affect chromium plating in a reliable, safe manner. Each process tank is equipped with temperature, level and conductivity sensors supplying analog outputs. Valves and pumps output discrete signals indicating on/off or open/closed. A pressure sensor in the main vertical stack and a temperature sensor in the drain sump provide early warning of spills or leaks. Flow is monitored with an ultrasonic instrument and controlled by a modulating butterfly valve in a return leg from the main vertical stack to the process tank. Safety interlocks between the process plumbing subsystem and the rectifier controls as well as a number of event sensing routines ensure that potentially dangerous situations are detected and corrected before damage or personal injury occur.

Operator interface with the control system is provided by an Advisor II process monitor. Identification of plating process parameters as well as a graphical representation of system operation is provided on a color CRT. System alarms are identified and cleared through this interface. The Advisor II is an old system and somewhat slow by today's standards but proven to be a reliable user interface.

Expansion of the rinse water recovery system, the addition of an on-line autotitrator for solution analysis, and an ultrasonic method for on-line measurement of chromium thickness has outstripped the capability of the existing control system. The Advisor II is being replaced with the Cimplicity control package from GE Fanuc running on a 486 PC imbedded in a VME rack. A GE Fanuc 90/70 PLC will be used in conjunction with the A/B 2/30 to provide extensive control and system monitoring capability.

HAZARDOUS WASTE MANAGEMENT

Reduction of hazardous wastes generated during chromium plating is a major advantage of vessel plating over immersion plating. Reduced air emissions due to the closed nature of the system are inherent, however the potential for rinse water reduction requires some engineering in order to fully exploit this potential. Water rinsing occurs between each process step and after the chromium plating process. Fresh water is fed into the main vertical stack under line pressure and flows through the tube, into the caustic/polish return line and to the floor drain which leads to an on-site waste treatment facility. Initial interest in rinse water reduction was focused exclusively on the chromium plating rinse waters. After the chromium plating cycle the rinse water is diverted to the chromium return line rather than the caustic/polish line. This does not return directly to the process tank but is instead diverted to the 300 gallon holding tank mentioned earlier. Diversion of the first 300 gallons of rinse water reduces the concentration of chromium in the rinse water which eventually goes to drain by approximately 80 percent. This captured rinse water is later used for solution make-up. Application of this method to the caustic cleaner and electropolish solutions is not practical due to the lack of sufficient water loss to the caustic tank and the incompatibility of water with the electropolish solution.

A rinse water recovery system applicable to all three solutions is shown in Fig. 3. The chromium rinse recovery loop only is shown here for clarity. Operation of this closed loop rinse is conceptually very simple. Rinse water is pumped from tank #1 though the tube and back to tank #1. A conductivity sensor in the rinse tank indicates when the rinse water has reached an equilibrium concentration. At this point valves 1 & 4 close and 2 & 5 open, pumping water from tank #2 though the tube and back to tank #2. Steady state conductivity in tank #2 moves the sequence to tank #3. Rinse tank #1 is now dumped to the process tank for make-up. Tank #2 is pumped to tank #1 and tank #3 is pumped to tank #2. Tank #3 is filled with fresh water and the tube rinsed a fourth time from tank #3. This system eliminates drag-out loss while providing adequate rinsing. Addition of evaporators and purification equipment make this system applicable to recovery of caustic and electropolish rinse waters.

OPERATIONS

Assembly of the tube, anode and sensors takes approximately one hour. Definition of desired plating parameters then allows the PLC to execute the plating process as previously described. Operator intervention is only required if a hardware malfunction occurs. Set-up time is roughly equivalent to the time required to fixture a tube for immersion plating, however in the immersion process the tube is moved ten times before it reaches the chromium plating operation. Vessel plating does not require the tube to move at all until the plating process is complete. During seven years of operation including over 60 plating runs, only two plating runs have been aborted due to equipment malfunction.

Several plating runs were executed to characterize the relationship between flow rate and current density to the mechanical properties of the chromium plate, the plating rate and the distribution of the plate (taper). These runs also served to verify previous laboratory testing. Variations in current density and to a lesser extent flow rate had an impact on the plating rate with plating rates as high as 0.005 in/hr being achieved. Variations in hardness values were observed with varying current density, as would be expected, however variations in flow rate also effected chromium hardness. Detailed correlations between these process parameters and plate qualities are considered sensitive manufacturing technology.

Subsequent to system characterization a number of tubes were plated with LC chromium and one with conventional HC chromium. These tubes are currently in firing tests.

COMMERCIAL APPLICATIONS

The vessel plating process can replace immersion plating wherever aqueous solutions are used for electrodeposition on long cylinders, either ID or OD. The work done here on chromium can be easily transferred to commercial items such as hydraulic cylinders, pipe used for handling abrasive slurries or aggressive chemicals, reaction vessels and mixing equipment. Conventional HC or LC chromium can be applied depending on the performance criteria for the particular application. Reduced plating times and elimination of hexavalent chromium waste can have a positive impact on production costs.

There is evidence to suggest that lead electroplated on copper forms an anode superior to the current casting or burning process. Plating bath composition and solution velocities required to obtain these desirable properties makes vessel plating the only viable method of fabrication.

Recent developments in the area of sputtering depositions have developed a need for long sputtering targets with heavy, uniform deposits of chromium. Here again vessel plating is the only viable fabrication method.

CONCLUSIONS

Various metals and alloys have been deposited using Vessel Plating Technology including copper, nickel, zinc, and lead. Any material which can be electrodeposited from aqueous solution can exploit this technology. Cathode configuration is somewhat restricted to simple geometries due to the flow rates required however, innovative design has made such operations as electroforming electrical circuits from copper possible.[3] In the current atmosphere of environmental regulation the potential for hazardous waste reduction could make Vessel Plating the predominant electroplating process of the future.

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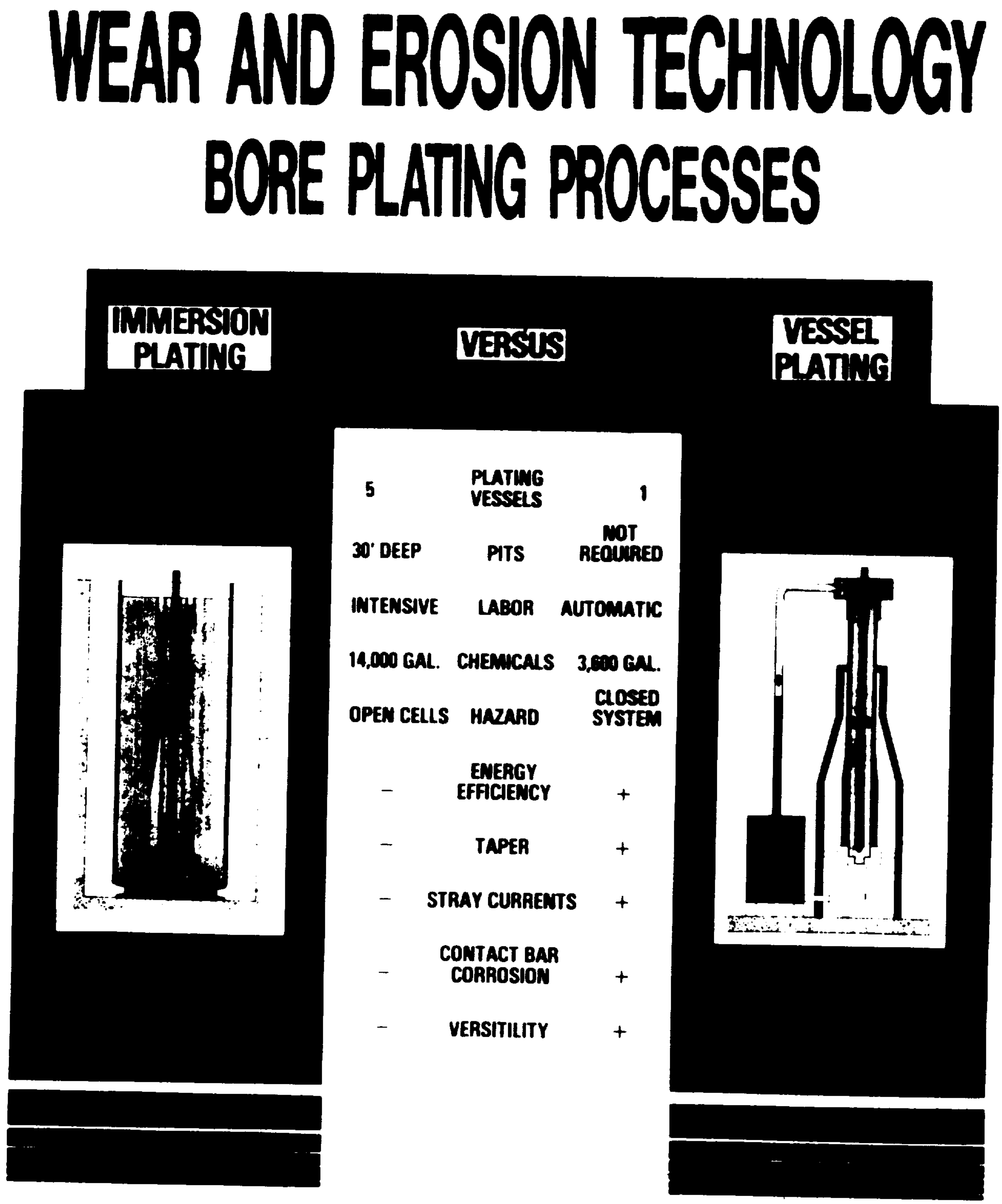
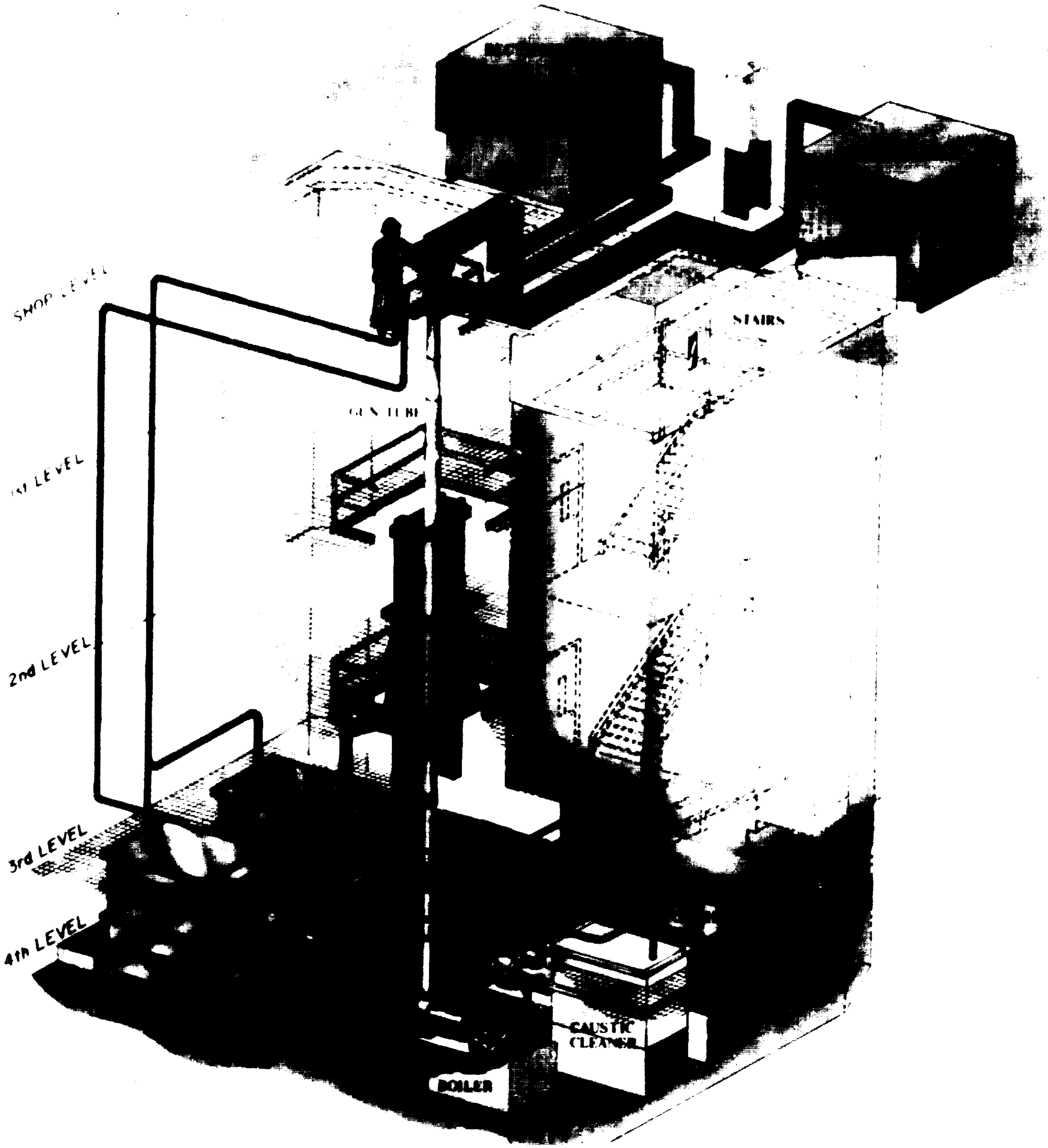


WEAR AND EROSION TECHNOLOGY
BORE PLATING PROCESSES
IMMERSION PLATING
VERSUS
VESSEL PLATING
5 PLATING VESSELS 1
30' DEEP PITS NOT REQUIRED
INTENSIVE LABOR AUTOMATIC
14,000 GAL. CHEMICALS 3,600 GAL.
OPEN CELLS HAZARD CLOSED SYSTEM
– ENERGY EFFICIENCY +
– TAPER +
– STRAY CURRENTS +
– CONTACT BAR CORROSION +
– VERSITILITY +

Figure 1



VESSEL PLATING FACILITY - BLDG 110

Figure 2

RINSE WATER RECOVERY SYSTEM

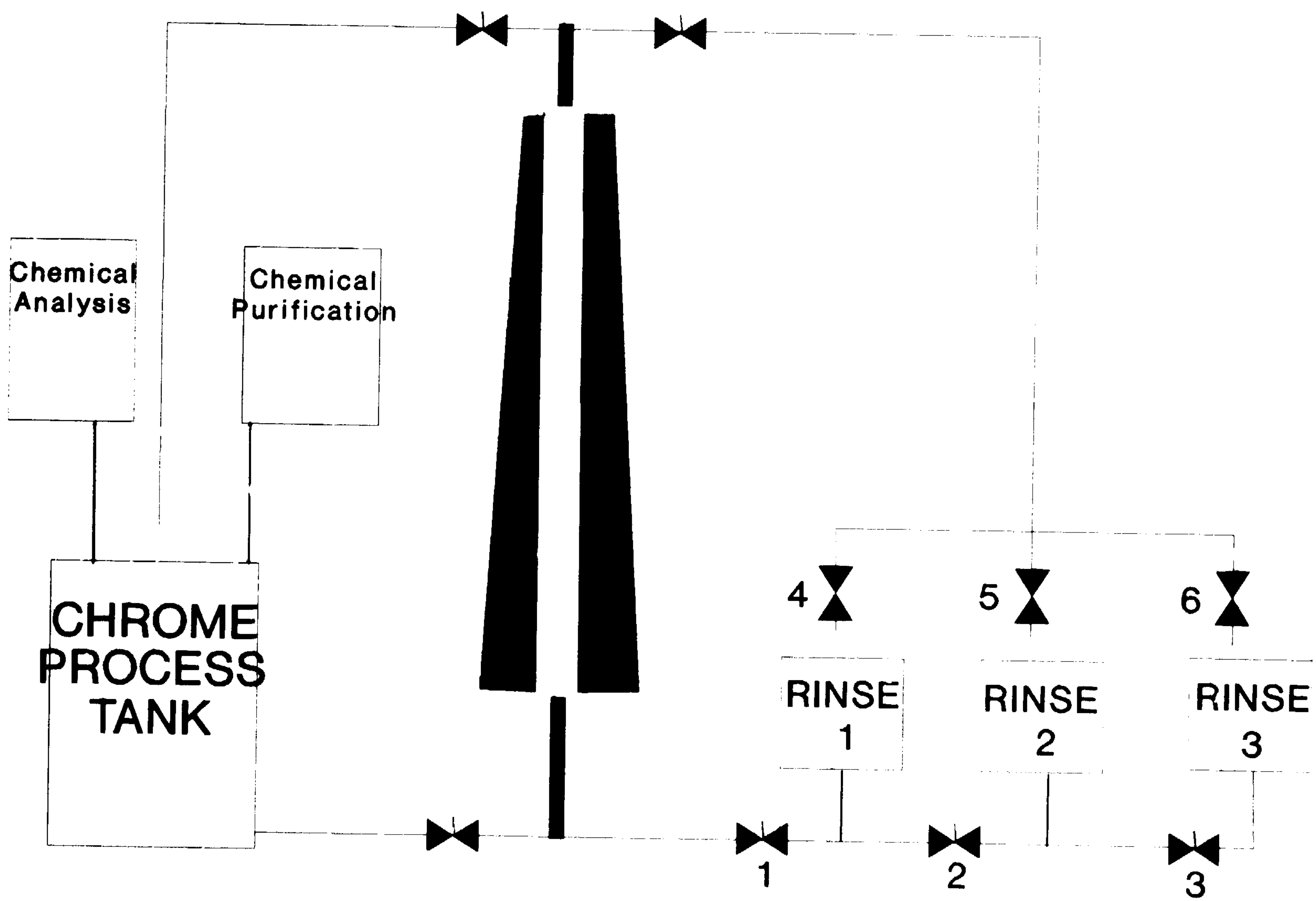


FIG. 3