UNITED STATES DEPARTMENT OF ENERGY (DOE)

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ANNOUNCEMENT

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3. OTHER IDENTIFYING NUMBER(s)

B. Recipient/Contractor

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☒ 1. TECHNICAL REPORT

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☐ 2. CONFERENCE PAPER/PROCEEDINGS

Conference Information (title, location, dates)

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a. TYPE: ☐ Announcement Citation Only

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☐ OTHER, SPECIFY

G. STI Product Reporting Period (mm/dd/yyyy)

09/17/1998

Thru

03/31/2005

H. Sponsoring DOE Program Office

DOE Golden

I. Subject Categories (list primary one first)

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Keywords

Inert Anode; Aluminum Reduction

J. Description/Abstract

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Organization -for Northwest Aluminum Technology

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- ☐ 1. THIS DELIVERABLE COMPLETES ALL
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Part 1: J. - Description/Abstract

The production of aluminum metal by low temperature electrolysis utilizing metal non-consumable anodes and ceramic cathodes was extensively investigated. Tests were performed with traditional sodium fluoride - aluminum fluoride composition electrolytes, potassium fluoride - aluminum fluoride electrolytes, and potassium fluoride - sodium fluoride - aluminum fluoride electrolytes. All of the Essential First-Tier Requirements of the joint 1998 DOE-Aluminum Industry Inert Anode Road Map were achieved and those items yet to be resolved for commercialization of this technology were identified. Methods for the fabrication and welding of metal alloy anodes were developed and tested. The potential saving of energy and energy costs were determined and potential environmental benefits verified.

Inert Anode Metal Life in Low Temperature Reduction Process

Final Technical Report

Project Period: September 17, 1998 through March 31, 2005

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Other Partners: LLNL, CSIRO, SINTEF, Oregon State University

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Abstract:

The production of aluminum metal by low temperature electrolysis utilizing metal non-consumable anodes and ceramic cathodes was extensively investigated. Tests were performed with traditional sodium fluoride - aluminum fluoride composition electrolytes, potassium fluoride - aluminum fluoride electrolytes, and potassium fluoride - sodium fluoride - aluminum fluoride electrolytes. All of the Essential First-Tier Requirements of the joint 1998 DOE-Aluminum Industry Inert Anode Road Map were achieved and those items yet to be resolved for commercialization of this technology were identified. Methods for the fabrication and welding of metal alloy anodes were developed and tested. The potential saving of energy and energy costs were determined and potential environmental benefits verified.

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Executive Summary:

This report summarizes Northwest Aluminum Technology's (NAT) accomplishments on Inert Anode Development under DOE Grant DE-FC36-98ID-13662 and identifies the additional research and development needs necessary to convert Low Temperature Inert Anode aluminum electrolysis into a commercially viable process. The report is divided into four major sections. The first section summarizes the results of the basic scientific research performed by Northwest Aluminum Technology's Seattle laboratories. The second section summarizes the progress achieved in continuing development activities performed at the Goldendale Aluminum and Northwest Aluminum primary reduction plants. The third section identifies the key elements of the DOE - Aluminum Industry jointly-developed Inert Anode Roadmap and compares these requirements to results achieved. The fourth section of the report identifies the developments that will be necessary to bring the process to commercial viability and the potential benefits in energy savings, environmental improvements, capital investment, and energy costs that may be achieved by successful development of the technology.

All initial work on the Low Temperature Aluminum Reduction utilizing non-consumable Metal Anodes was performed in NAT's Seattle Laboratories. The work on this project was a continuation of basic research performed on a prior grant and based on patents issued to Theodore Beck for electrolytic aluminum production utilizing metal alloy inert anodes with active anodic linings operating with an alumina slurry in a sodium fluoride - aluminum fluoride bath. NAT's Seattle laboratory continued Beck's work with bench scale electrolytic cells of 10 ampere capacity constructed of copper-nickel-iron alloy with titanium diboride ceramic cathodes and operated in a NaF-AlF₃ electrolytic bath with a slurry of fine (nominal 1 micron size) alumina particles. Electrolysis tests were performed in the 10-amp cells and in later 200 to 300 ampere cells to identify the optimal anode alloy and corrosion mechanisms. In conjunction with the laboratory electrolysis tests, metallurgical analyses were performed utilizing X-ray diffraction, optical microscopy, scanning electron microscopy, energy dispersive spectrography, microprobe, and inductively coupled plasma fluorescence by Oregon State University, CSIRO of Australia, and the plant laboratories of Goldendale Aluminum in Washington and Northwest Aluminum in Oregon.

In early 2000, parallel development activities were commenced with 200-amp to 300-amp bench scale cells in an existing pilot plant at the Goldendale Aluminum smelter and subsequently moved to the Northwest Aluminum smelter with the

construction of a new development facility commissioned in early 2002. The Seattle laboratory continued to perform and monitor basic research while the smelter development facilities addressed practical methods of constructing, feeding, tapping, and controlling the inert anode cell with the objective of designing and operating a larger pilot cell of 5,000-ampere capacity.

Achievements of these research and development efforts are summarized as follows:

- Operation of bench cells in the 200 to 300 ampere range with vertically oriented metal anodes and TiB_2 cathodes.
- Continuous operation of bench cells in excess of 300 hours.
- Operation of bench cells in excess of 94% overall current efficiency in long duration runs.
- Production of aluminum metal quality exceeding 99.9% purity with respect to the elements of the anodes and cathodes utilizing conventional smelter raw materials.
- Casting and fabrication of anode plates in excess of two feet by two feet cross-section and assembling complex shapes by welding with conventional equipment.
- Simple and reliable methods of sealing, feeding, and emissions scrubbing crustless low temperature inert anode cells.
- Development of methods to tap a vertically-oriented inert anode cell with an active bottom using conventional smelter tapping equipment.
- Construction and preliminary operation of larger pilot cells up to 5,000 amperes.
- Successful achievement of all of the First-Tier Essential requirements of the joint DOE-Aluminum Industry Inert Anode Road Map.

Items necessary for commercialization yet to be resolved include:

- Structurally superior rigid wettable cathodes.
- Enhanced protection of anode and cathode components where they penetrate the bath line.
- Development of improved bath-resistant refractory for cell linings.

The Seattle laboratory was shut down and the development activity at Golden-Northwest smelters severely curtailed when additional funds were not appropriated to this grant and Golden-Northwest (including NAT) went into Chapter 11 bankruptcy in December 2003.

Section 1 - Basic Research Tasks performed by the Seattle Laboratory

Narrative discussion of Seattle Laboratories work:

An application for Federal Assistance was submitted by Northwest Aluminum Technologies (NAT) on March 16, 1998 and Grant DE-FC07-98ID13662 was approved on 17 September 1998. The proposal was submitted in collaboration with Brooks Rand, Ltd. (BRL), Electrochemical Technology Corp (ETC), and Oregon State University (OSU) to develop a new primary aluminum production process. The proposed technology was a low temperature electrolyte bath saturated with alumina and utilizing inert metal anodes with an anodic cell liner and titanium diboride ceramic cathodes.

The proposed process was based on four patents of ETC and BRL on electrolytic compositions, suspended alumina cell designs, and metal anode composition. The research plan was to fabricate metal anodes in several ways and test these during relatively long runs in 10-ampere cells and 300-ampere cells to develop the design and materials necessary to construct and operate a 5,000-ampere demonstration cell leading to commercialization of the technology. The proposed program essentially followed the "Inert Anode Roadmap" jointly prepared by the Department of Energy, the Aluminum Association, and nine aluminum producers published in February 1998.

Initial work was performed in space leased from the Seattle laboratories of BRL and subsequently moved to a separate nearby facility as efforts were expanded. The initial efforts were concentrated on the 10-ampere bench top cell to develop a conceptual model of anode activity of the preferred alloy compositions. The basic arrangement for these tests consisted of an alumina container, an anode of the alloys tested placed on the bottom of the container and a cathode, normally of TiB_2 , suspended above the bottom anode. To allow rapid fabrication and testing of different ratios of the proposed copper-nickel-iron anode alloys, anodes were fabricated in the laboratory by hot pressing and sintering pure powders of the metals into anode disks. The bath utilized was a ratio of sodium fluoride and aluminum fluoride that demonstrates a very sharp eutectic at approximately 44 to 45 mole % aluminum fluoride with a melting point below 740 degrees C. This bath was modified with the addition of fine alumina (nominal 1 micron particle size) in the range of 10% by weight, well in excess of the approximately 3% maximum solubility of alumina in the bath at this temperature range. Due to the generation of oxygen bubbles on the bottom anode, the excess alumina was retained as slurry in the bath by the stirring action of the generated oxygen.

Since the cathode was suspended above the active anode, the durations of these tests were limited to approximately five hours to avoid metal dripping from the cathode back onto the anode, where it would re-oxidize and react with the anode alloys.

While this work was proceeding, air-oxidation testing was performed on various sintered and cast anode alloys, then analyzed by OSU utilizing X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). During the first six months of the project, tests on sintered anodes were completed. Four different anode compositions were tested in triplicate in 5-hour runs at 0.5 amps/cm^2 with a nominal anode-cathode distance (ACD) of 1.27 cm. Professor M. Kassner at OSU analyzed anode specimens from these tests by SEM and EDS. Also during this period, the intermittent issue of non-wetting of the titanium diboride cathodes was addressed and procedures of bath preparation developed to overcome this problem.

During the electrolysis testing with the 10-amp cell, a 300-amp cell was constructed with a cast liner of copper-nickel-iron alloy and equipped with multiple interior anodes and TiB_2 cathodes for tests to develop methods of metal removal so that electrolysis could be sustained for longer runs than the five hours. Metal removal from a cell while in operation whose entire interior is anodic posed a challenging problem but was necessary to allow longer testing and development of larger cells leading to commercialization. As with the 10-amp cell, this cell was operated on a eutectic NaF-AlF_3 bath with a slurry of fine alumina that was hand-fed to maintain a concentration of approximately 10%.

Cast alloy anodes of the same compositions tested by sintering were prepared by Northwest Aluminum in The Dalles, Oregon utilizing heated graphite molds while additional anodes and cell liners were fabricated through investment casting by SeaCast in Marysville, Washington. Upon completion of the sintered anode tests in the 10-amp cell, cast anode specimens were tested in the same conditions and found to be generally superior in corrosion resistance and produced metal purity to sintered anodes.

Numerous attempts to perform the continuous removal of aluminum from the cathodes of the 300-ampere cell were performed without success and the cathodes were redesigned to provide for a metal reservoir within the cathode to assist in this process. This concept was tested in the 10-ampere cell. This necessitated redesign of the 300-ampere cell and the fabrication of new cathodes became a

significant delaying factor in the overall schedule. Air oxidation test analyses at Northwest Aluminum identified an anode composition that exhibited superior corrosion characteristics and steps were taken to fabricate cell liners and anodes from this material. By one year into the project, sintered anode specimens were abandoned in favor of cast specimens.

An alternate method of metal removal from the cathodes of the 300-amp cell was demonstrated that would allow longer-term operation, although this manual time-consuming method was not feasible for larger cells or commercialization. During this period, anode performance in the 5-hour test runs of both the 10-ampere cell and the 300-ampere cell was quite good and at or near quality and energy targets. 54 electrolysis tests (including replicates) were completed in the 10-ampere cell on 16 different anode alloy descriptions. Seven different compositions of sintered anodes and nine compositions of cast anodes were tested. A new laboratory facility with electrical and space facilities for larger cells was constructed and occupied at the end of 1999. At the same time, the decision was made to equip an existing pilot facility at the Goldendale Aluminum smelter to run parallel development to the research efforts in Seattle. The operations and results of this parallel effort are discussed later in this report.

After relocation to the new NAT laboratory in Seattle, 53 electrolysis tests were performed. These included tests outside of the standard matrix by varying bath chemistry, alumina feedstock, cathode materials, and other factors. Some of these tests were in the 300-amp cell. At Northwest Aluminum in The Dalles, OR work began on the development of techniques to weld the anode alloys of greatest interest and after several attempts, promising results were achieved. Casting of the most promising alloy continued to be performed by both Northwest Aluminum and SeaCast. By June, 2000, 56 additional electrolysis tests were conducted in the Seattle laboratory, all in the 10-amp cell, and a further 47 10-amp cell electrolysis tests were conducted by September 2000. 100-hour testing was commenced during this period with a 12-hour test completed without problems. A second test of 18 hours duration was halted due to problems other than metal removal. By January 2001, 10 additional tests in the 10-amp cell were conducted with one of these of 100 hours duration. The overall current efficiency for the 100-hour test was 90% and, for the majority of the test duration, the metal produced was of commercial purity. Nine electrolyses were conducted in the 300 amp cell at 200 amps. The longest of these was 42.5 hours and stopped due to a fractured cathode.

By the end of 2000, characterization of anode samples by SEM, Microprobe, and XRD by CSIRO in Australia were beginning to yield definitive information about corrosion layers formed on the anodes and this work was continued with additional anode samples from electrolysis runs.

Additional work in the 10-amp cell continued to study conditions leading to accelerated corrosion (blister corrosion) and of the effects of slurry content on cell operation. The aluminum extraction method to allow longer runs was proven, although it was not suitable for pilot or large cell operations and three extended tests were conducted in the 200-ampere cell lasting 52, 57, and 89 hours respectively. Current efficiencies were 82.9%, 86.8%, and 83.7% for these runs. The first test was halted when one of the external oven heaters failed. In the second test, the particular anode alloy tested developed high resistance and was replaced several times before the run was terminated. The third test was terminated due to problems related to bath ratio. With no effective way to rapidly determine bath ratio during the operation of the 200-ampere cell, the adjustment of bath ratio to compensate for losses of fluoride to the fume extraction and for sodium content in the ore was by dead reckoning. In the first quarter of 2001, it was clear that delays in developing aluminum removal techniques suitable for the larger cell had delayed the project and an extension request was submitted.

During the remainder of 2001, the Seattle laboratory concentrated on anode compositions, resistance to corrosion, and process control procedures utilizing a fine alumina slurry. Alternate cell arrangement and metal removal procedures incorporated by the parallel development activities at Goldendale succeeded in achieving the 100-hour milestone for operation of the 200-ampere cell and runs of this duration became routine at that facility, allowing the Seattle laboratory to concentrate on basic research. The metal removal procedures at Goldendale were suitable for larger cells and design work for the 5,000 amp cell was commenced based on this development. Eight tests were run in Seattle using copper anodes rather than alloy anodes and one test was performed with an inactive metal cell liner. Seven tests were conducted in the laboratory 200-amp cell by the end of September with the longest of these being 73 hours.

By the end of 2001, results had been obtained for the solubility of iron oxides under LTE conditions and results were in hand from the impedance spectroscopy and resistometry tests and were in evaluation. A bath ratio probe was developed and tested in the laboratory and the specifications for a hand-held version were completed. Several runs of the 200-amp cell lasting 100 hours were performed

using the laboratory hand-removal techniques of the metal produced. A supplement to the cooperative agreement with DOE was approved in January 2002.

At the end of 2001, the parallel development at the Goldendale pilot plant was shut down and personnel and equipment relocated to a new facility constructed at the Northwest Aluminum smelter in The Dalles. This facility was commissioned in February 2002 and portions of the anode alloy testing and development was reassigned to that location. The Seattle laboratory developed a novel "frozen cell" approach to analyze the cathode environment and the electrolyte composition. Work continued on a hand-held fluoride probe to allow in-operation determination of bath ratio. Alumina dissolution studies were commissioned to study the effects of particle size and phase (alpha versus gamma) on alumina dissolution rates in the low-temperature bath composition. A contract was completed with the University of Greenwich in the UK and Process Engineering Resources of Salt Lake to utilize their PHYSICA modeling package to examine bath flows due to convection and oxygen generation plus the distribution of alumina in slurry and non-slurry conditions to prepare for final design of the 5,000-ampere cell.

During 2002, the Seattle laboratory continued to work on frozen cell analyses, bath ratio probes, and alumina dissolution studies. Electrolysis in the laboratory's 200-amp and 10-amp cells continued. The AC frequency component of impressed cell voltage was studied and did not yield any useful information. Methods of improving the performance of nickel scale were tried and abandoned. Tests with potassium fluoride - aluminum fluoride bath and combinations of KF-NaF-AlF₃ baths were performed with promising results in terms of metal purity and anode corrosion. The completion of the alumina dissolution studies proved that commercial smelter grade sandy alumina with high gamma phase had a much higher dissolution rate than the fine, high alpha alumina used in the slurry cells, although the ultimate solubility was no different. Several grades of alumina were tested in the different variations of the baths under examination. As expected, the solubility of alumina in the bath decreased with increased calcium and increased with potassium fluoride and lithium fluoride additions. The dissolution rates were very dependent upon the calcining temperature and surface area of the alumina. A prototype fluoride probe was delivered but required modification.

In 2003, laboratory work continued on KF-NaF-AlF₃ bath combinations and these continued to show superior performance in metal purity and process control. Commercial grade metal was produced utilizing copper anodes in baths with suf

ficient KF composition. Work on the fluoride probe was abandoned after several additional tests and the use of a wider range of electrolytes being tested greatly reduced the usefulness of this potential tool. A simple, two dimensional hydrodynamic flow model from the University of Greenwich and Process Engineering was delivered for the 200-amp cell at the Northwest Aluminum Development line and the 5,000-amp cell as designed. These models in conjunction with alumina dissolution studies verified that the flow turbulence was sufficient to avoid any significant variation in alumina concentration within the baths of these cells. Further work on a more complex model was put on hold as the results from this modeling would not be received until long after the planned commissioning of the 5,000 amp cell and therefore would not be useful in its initial design.

An extension was executed for the project to extend the completion date until March 31, 2004.

Metallurgical testing continued by outside contractor, primarily Oregon State University. An extensive series of tests was performed on a wide range of copper-nickel-iron alloys cast by the Northwest Aluminum development facility and outside foundries. These tests showed that all of the as-cast alloys under consideration freeze into two or more distinct phases on a microscopic level. Many of the alloys can be homogenized to a uniform phase, but exposure to temperatures in the ranges used by the LTE technology for periods of up to 400 hours resulted in de-homogenization back to two or more distinctly different phases. These were not necessarily the same phases that existed before homogenization. The conclusion from these studies did not show any clear advantage for homogenization, although more study in this area appears warranted.

The Seattle laboratory continued to work on alternate metal removal methods for the active liner slurry cell and the viability of a third method of metal removal was demonstrated in a multi-tapping cycle test. LLNL completed preliminary weld tests on one anode alloy with electron beam and high power laser. Both yielded successful welds. The laser penetration depth was limited and introduced more defects than the electron beam method.

Due to continued financial difficulties of the aluminum smelters in the Pacific Northwest, shortage of funds by Northwest Aluminum Technologies, and lack of appropriation of grant funds for the DOE share of the project costs, the Seattle Laboratory was closed in the fall of 2003 and remaining personnel and testing transferred to the development facility at the Northwest Aluminum smelter in The Dalles. As an affiliate of Goldendale Aluminum, NAT filed for Chapter 11 bank

ruptcy on December 23, 2003. Layoffs, reassignments, and curtailment of experimental aspects of the project accompanied this filing. The development work underway at The Dalles was greatly reduced. A project extension was requested and approved to extend the completion date of the project to March 31, 2005. As of May 2004, Dr. Craig Brown was no longer an employee of NAT and no longer associated with the project. All remaining activities past that date were accomplished by personnel at the development facility in The Dalles. By the March 31, 2005 extended completion date, NAT was still under Chapter 11 reorganization and no long range decisions have been made regarding continuation of inert anode research and development.

Arrangement of Equipment and Adopted procedures:

10-amp cell:

The general arrangement of the Seattle 10-amp laboratory cell consisted of an externally heated alumina container with a metal alloy anode covering the bottom of the container and a titanium diboride cathode suspended above the anode. Electrical feed to the bottom anode was by a copper wire contained in an alumina sleeve. The cathode projected above the surface of the electrolyte and was suspended by and electrically connected to a stainless steel frame. The cathode did not shadow the entire surface of the bottom anode. Typically, the cell was run at a current density of 0.5 amps/cm² based on the upper anode surface. The ACD to the bottom of the cathode was typically 1.27 cm (1/2 inch). The entire assembly was housed in a cabinet with ventilation to collect fluoride fumes off-gassed from the cell.

Fine-grained alumina of approximately 1 micron in diameter and of low surface area (approximately 1½ square meters per gram, essentially spherical) was hand fed to the cell during operation every 15 minutes at a rate equal to the estimated current efficiency to maintain a total of 10% alumina in the cell by weight. The estimated solubility limit of alumina in the nominal 740° C to 760° C electrolyte was 3% by weight.

For most of the tests utilizing the 10-amp cell, the electrolyte was a eutectic composition of NaF-AlF₃ at 44 to 45 mole percent AlF₃. Figure 1 is a copy of the sodium fluoride-aluminum fluoride curve versus temperature and mole percentage aluminum fluoride concentration.

Figure 1 Phase diagram of the NaF - AlF_3 system

300-amp cell:

The general arrangement of the Seattle 200-amp to 300-amp laboratory cell consisted of an externally heated cast anode alloy container with two titanium diboride cathode plates and one center anode plate suspended in the container. In this arrangement, the cathode plates were opposed by the long sides of the container on one side and the center anode plate on the other side. The entire inner surface of the container functioned as anode. Generally, the spacing between the sides of the container and the cathode plates was at the typical ACD of 1.27 cm and the spacing between the center anode plate and the cathodes was also at the 1.27 cm ACD, although the sides of the container were slightly sloped for casting considerations. The distances of the ends of the container were also typically 1.27 cm from the edges of the cathode and the bottoms of the cathode were spaced 1.27 cm above the bottom surface of the container. Cur

rent density was typically 0.5 amps/cm^2 based on the surface area of the cathodes. This cell was also normally operated with the NaF-AlF₃ eutectic bath in the nominal 740° C to 760° C temperature range. These cells were also hand-fed with fine alumina on a 15-minute schedule to maintain the estimated 10% total alumina by weight. Some tests were run with an alumina container equipped with anode plates on the bottom and on the sides, but the majority of tests in the 200-ampere to 300-ampere range were with the active anodic metal alloy container.

Cell metal removal:

In either arrangement, the metal produced was held on the cathode plate by the surface tension of the liquid aluminum and the wettability of the TiB₂ cathode plates. After approximately five hours of operation, the amount of metal produced was sufficient to overcome the surface tension and allow a metal droplet to fall on the anodic bottom unless the operation was either terminated or metal removed. Initial operations of both cells were limited to five hours until methods of removing the metal could be developed.

Initial attempts to remove metal from the cathodes while in operation consisted of attempting to insert a small wettable tube of molybdenum or other relatively molten aluminum resistant material and vacuum the metal off of the surface. This was generally unsuccessful due to inability to heat the tube evenly to prevent metal from freezing or prevent suction of bath into the tube. The first successful metal removal technique consisted of "wicking" the metal from the surface of the cathodes with a tool fabricated from molybdenum foil leaves. The aluminum was drawn into the foil leaves by surface tension and while still molten, removed from the cell and shaken off by tapping on the sides of an external container. Although this procedure worked for laboratory purposes, it was a manual operation required on each cathode plate on a schedule of approximately every two hours. It also disrupted the cell operation since the molybdenum foil tool had to be inserted into the ACD distance between the cathode surface and an active anode face. Although the molybdenum was slowly consumed by alloying with the liquid aluminum, molybdenum was not an ordinary component of the anode, the cathode, or raw materials and this contamination was ignored for the purpose of anode and cathode corrosion evaluations.

Attempts were made to enhance the volume of metal by constructing hollow TiB_2 cathodes and allowing the surface tension to create a pool of metal inside of the hollow portion of the cathode. It was determined that with a spacing of approximately one centimeter between the inner sides of a hollow cathode, a pool of metal approximately three centimeters deep could be created. The advantage of this was that it extended the tapping intervals somewhat and also allowed metal removal without placing a disruptive conductor in the space between the anode and cathode surfaces. The fabrication of hollow cathodes was time-consuming and considerable additional expense, however, and manual attention was still required.

Later in the development process, hollow cathode 200-amp cells were equipped with wettable ceramic tubes into the metal reservoir. By retaining these tubes within the cell oven, it was proven that metal could be continuously gravity siphoned from the reservoir in the cathodes to an external container. This can function as a self-regulating device, since with sufficiently small diameter wetted tubes, the aluminum surface tension excludes the bath and metal drained over the side automatically based on the height of metal in the cathode pool and in the external reservoir. Although this process was proven as a research tool, it was deemed not practical for commercialization due to the expense and number of tubes involved, the necessity of maintaining electrical isolation, and the small size of the tubes which could lead to frequent plugging if any particles of frozen bath existed.

Cell preparation:

Based on prior research in which difficulty was experienced in initial wetting of the TiB_2 cathodes, preparation of the cell for electrolysis included pre-treating the bath by melting NaF and AlF_3 powders in the proper ratio, then adding a small amount of aluminum metal (normally aluminum foil) to the molten bath to react and precipitate out any impurities. Following this treatment, a small amount of alumina was added to the melt to insure that it was at saturation, then the prepared bath was allowed to sit for several hours until all solids precipitated and the bath was visually clear. The clear bath was then decanted, allowed to freeze, and then crushed to the granular powder used to charge the cell for startup.

The cell was prepared by mounting the anodes, cathodes, and electrical connectors; placing the cell in its run oven; filling it with the prepared bath

powder; then heating the cell and its internals immersed in the bath powders until the bath melted and was to proper temperature. At this point, electrolysis was commenced. This method of startup insured that the bath was clean of contaminants such as sulfur, that the cathode was protected from oxidation, and that the cathode upheal rate was sufficiently slow so as not to thermally stress the fragile TiB_2 .

Operational monitoring:

Cell voltage, cell temperature, rectifier current, and the voltage on the reference electrode were monitored continuously throughout a test run. These cell data were collected and converted to digital information and a display screen showing a graph of the cell voltage versus time was displayed on the screen at all times for operator information. Cell operators recorded the time and amount of all alumina additions, any bath additions, the time and amount of all metal tapped, and any other significant events in a manual log record of each test run. Bath samples were collected at regular intervals throughout the run and saved for laboratory analyses. At the completion of the run, the manual log and the data records were saved with the cross-referenced identification of the anode and cathode used in the run along with calculated current efficiencies and specimens of the anodes used and metal produced.

Cathodes were reused from run to run unless there was a significant issue with the cathodes, such as an unusual deposit, a fracture, or delamination, in which case the cathode specimen was also saved for later analyses.

For both sizes of cells, fluoride emissions were collected within the laboratory hooding but the amount of fluoride compared to the exhaust volume of the hooding was such that no reliable measurements could be made to verify the amount of fluoride lost from the process. The Seattle laboratory was not equipped with any reliable method of determining the ratio of sodium fluoride to aluminum fluoride during the run, so for the longer runs aluminum fluoride additions were made by dead reckoning based on historical results of prior runs and the known amount of sodium in additives to the cell during the run. To maintain bath height, extra prepared bath powders were added to the run as necessary to account for losses due to bath sampling and metal tapping.

The inability to monitor bath ratio during operation created a severe handicap for runs upwards of 100 hours in duration and several longer runs were terminated prematurely due to bath ratio problems that created unexpected bath freeze zones within the cell. To resolve this problem, a series of tests were run to develop a bath ratio probe based on the response of a reference cathode immersed in the bath and separately powered. The data from these tests were correlated to the subsequent external laboratory analyses of alumina content and bath ratios, adjusted for temperature, and analyzed to determine the effect of the ratio on probe response. Initially, a program was developed on a laboratory computer to translate the results into a bath ratio indicator that was used during a run to verify the dead-reckoning calculations for aluminum fluoride additions. Specifications were written and a contract let to design and fabricate a battery-powered hand-held probe to give a direct readout of the NaF-AlF₃ ratio. After this product was delivered and several attempts made to modify it to work properly, the instrument was abandoned.

Post-run bath analyses and metal analyses were performed by the plant laboratory of the Goldendale Aluminum smelter, which had the necessary equipment and personnel to do the analyses and interpret the results. These results were generally received two to three weeks following a run, so in many cases, several subsequent runs were already performed before the data from a run was received and evaluated.

Photos & Graphs:

Figure 2 - Photo of 300-amp cell in operation

Figure 3 -One of the 300-amp cell cathodes at end of a run

Feeding alumina at 300-amp cell
Figure 4

Figure 5 - Cross-section through the 10-ampere cell (This is a view of the cut through a 10-amp cell frozen during electrolysis for analyses of cathode and bath compounds present during operation)

In the right hand photo of the frozen cell cross-section, there are three areas identified as “a”, “b”, and “c”. The following photos show the analyses of one of those areas.

Figure 6 - The photo to the right shows an element map of portion of area “b” with a region of interest marked as a black rectangle. On the following page, the profile of element concentration in the region of interest off of the cathode is displayed.

Figure 7 - This photo is a map of the element concentration in the region of interest outlined in Region "b" on the previous page.

As can be observed from this map, there is a concentration of sodium or depletion of fluoride in the zone just outside of the metal pad that existed on the cathode during electrolysis at the time of freezing.

These analyses confirm the observations of a cryolite or chiolite freeze on the metal pad of the 200-amp cell at Goldendale during the first 100-hour run at that location. This freeze and its avoidance are discussed in a subsequent section of this report.

Section 2 - Development Activities at the Goldendale Pilot Plant and The Dalles Development Line:

Narrative Discussion of Development Work:

The development plan was to accomplish the assigned tasks in four phases. Phase 1 was to address the physical issue of how to seal, feed, scrub, and remove metal from the cell without regard to production efficiency or metal quality. Phase 2 was to address the process modifications necessary to achieve long-term operation with the physical arrangements identified in Phase 1. Phase 3 was to construct a new, larger development facility and train smelter personnel in the operation of an inert anode cell. Additional anode composition development and metal quality targets were subsequently added to this phase. Phase 4 was to construct and operate a larger development cell of 5,000 amperes capacity for an extended period.

Phase 1 - Physical Issues:

Initial development commenced in an existing pilot plant constructed for a different purpose at the Goldendale Aluminum Smelter, Goldendale, Washington. Inert anode work at this facility commenced in January of 2000 with the placement of orders for rectifier equipment, oven compo

nents, and instrumentation. An excess cast metal cell liner of an alloy no longer under consideration was provided by the Seattle Laboratory to act as an anodic container and internal anodes of a different cast alloy were provided by the metallurgical department of the Northwest Aluminum smelter at The Dalles, Oregon. Seattle research up to this point in time had concentrated on the utilization of extremely fine (approximately 1-micron) alumina batch-fed into the anodic container to maintain an alumina slurry. This type of alumina had a very low fluoride gas adsorption affinity and a low adsorption surface area of approximately 1.5 m² per gram. The cathodes used at the Seattle Laboratory were of titanium diboride ceramic, which was expensive to fabricate and quite fragile to thermal shock. Due to the anodic container, operating times were limited to the range of 5 to 6 hours until a method to remove produced metal from the cathode could be developed that would allow longer operation.

Since the initial assignment was to resolve the physical issues of hooding, feeding, scrubbing, and tapping, initial cell tests at the pilot plant utilized titanium metal for cathodes due to its relatively low cost to procure and ease of fabrication into complex shapes. The first 48 runs of the nominal 300-ampere cell at the pilot plant utilized titanium metal for cathodes.

The first test run at the pilot plant was performed on March 23, 2000. This run was in a sealed cell with automatic feed, fume extraction, and fume scrubbing. The run was only 2½ hours in duration due to failure of the cathode electrical connections inside of the sealed cell at 740 degrees C. This run was performed on smelter-grade sandy alumina available at the Goldendale smelter as this alumina was readily metered with automatic equipment and had a large adsorptive surface area for fluoride (nominal 70 m² per gram). A novel approach to scrubbing was used on this first cell by withdrawing the off-gases through the feed tube of the cell so that the cell was equipped with its own individual dry scrubber. Although this run was of short duration, it proved the concept of automatic continuous feed and integral dry scrubbing for the crustless inert anode cell.

Subsequently, approximately one dozen additional runs of 5 to 6 hours maximum duration were performed with this first 300-amp setup after modifications were made to extend the cathode electrical connections external to the cell hooding. The duration of the runs was limited due to liquid aluminum buildup on the cathodes without any effective way of removing the metal except shutting down the cell. During this initial series of runs,

it was determined that the Seattle laboratory criteria of 10% alumina slurry could not be maintained with the coarser smelter grade alumina. A modified alumina consisting of dust collector fines from the smelter alumina handling system was then tested. This material was approximately 80% under 20 micron in particle size but still retained significant surface adsorption area. It was not analyzed for fluoride affinity. With this material, a 10% slurry could be maintained but the material was more difficult to feed with automatic equipment and did not show any significant process advantages over the smelter-grade sandy alumina. It was abandoned and most of the pilot plant runs were subsequently made utilizing sandy alumina from the smelters.

Due to the excessive shrinkage difficulties experienced by third-party foundries and The Dalles smelter metallurgist in casting the range of copper-nickel-iron alloy desired for the inert anode container, it was concluded that to construct a successful commercial-sized anodic container cell procedures would have to be developed to weld smaller plates of the alloy into large containers. For the next series of pilot plant runs, a nominal 300-amp cell of welded Cu-Ni-Fe was designed. Two of these were cast and fabricated in the Metallurgy Department of The Dalles smelter. Although four successful runs were performed in each of these containers, the welding failed on both due to difficulty in obtaining weld penetration without thermal cracking of the alloy at the edges of the heat-affected zone. Repairs were made to achieve seven additional runs on these containers, but the welds continued to be a failure point on these cells. During these 15 runs, cathode redesign to create a metal reservoir integral with the cathode was tested. This could be fabricated from the titanium cathodes in use, but would be prohibitively expensive to fabricate from the preferred titanium diboride cathode material. Later runs in this series experimented with the collection of produced metal in small alumina reservoirs placed below the cathode on the active bottom of the anodic cell.

Photos of this fabricated container and of the titanium cathode assemblies used are shown in a subsequent portion of this report.

As a result of the second series of runs, it was concluded that metal could be successfully collected in an insulated container placed in the bottom of an anodic cell. It was also concluded that fabrication of a large cell by welding of the then-preferred anode alloys would be problematic for the long, leak-free life necessary for a commercially viable cell.

The next series of 17 runs at the pilot plant concentrated on the collection of aluminum produced in the bottom of the cells. These runs were alternated between a cast, active anodic container and containers fabricated of dense alumina, insulated and non-anodic. Late in this series of runs, runs of extended length were attempted by removal of the collected metal during operation. Extended runs with the titanium metal cathodes proved infeasible as, after some 30 hours of operation, the produced aluminum alloyed with the titanium to the point that it was no longer liquid and would not drain to the collection receptacle. These runs proved that metal could be collected in an insulated reservoir on the bottom of a cell with an active bottom anode. The difficulty was that due to the close spacing of the anode and cathode plates in the cell ($\frac{1}{2}$ " to $\frac{3}{4}$ " ACD), the reservoir could not be large and would have to be tapped prohibitively often. The runs also proved that to achieve the then-desired milestone of 100 hours continuous operation, the titanium cathodes would have to be abandoned in favor of titanium diboride cathodes that do not significantly dissolve and alloy with the produced metal.

During this series, a cell design was conceived consisting of an inner container of dense alumina fitted in an outer container of dense alumina, and the inner container equipped with an active anode in the bottom. The bottom anode and inner alumina container were drilled with drain holes and the cathodes equipped with drain tips located approximately over the drain holes. This allowed the liquid aluminum produced to drip from the cathode, fall through the bottom anode and be collected in the bottom of the outer reservoir where it could be tapped by conventional siphon means. This concept was tested in a 12-hour run with a titanium cathode but the test was aborted because of problems with the metal viscosity due to alloying with the titanium.

Phase 2-Longer Operations:

Steps were taken to procure titanium diboride cathodes sized to fit the alumina containers that became standard for the pilot plant runs. The first titanium diboride cathode run was performed on August 8, 2001 for 48 hours. This run was in an inactive alumina container, with sandy alumina feed, and vertically oriented Cu-Ni-Fe anodes. The cell was sealed, continuously fed, and with integral fume collection and scrubbing. The drain tip of the cathode was maintained in constant contact with the aluminum

metal pad to avoid parasitic current. Metal was removed at 8-hour intervals by spooning from the bottom of the cell with a stainless steel spoon. Current efficiency for the run was 83.5% and was low due to re-oxidation of metal on the TiB_2 cathode riser at the bath line. The TiB_2 cathode was wetted with liquid aluminum and the surface tension of the metal on the cathode drew it to the surface of the bath, where it was free to re-burn at in the oxygen-containing foam on the surface of the bath.

Based on the experience of this test, the setup was reconfigured and the next run on August 21, 2001 was for the milestone 100 hours using the same setup. For all metal collection runs prior to this run, the cathode shape was always configured to maintain the metal produced at cathode potential to avoid any parasitic currents. If the metal pool is not at cathode potential but lying disconnected in the bottom of a cell, a current path exists from the bottom of the anodes to the metal pad and then back to the cathode plates. This path produces new metal on current entry from the anode but re-oxidizes the metal on its exit to the cathode and therefore is parasitic and reduces the efficiency of the cell. During the 100-hour run, a problem was experienced with a bath freeze on the cathodic metal pool. During the run, the cathode was raised to disconnect the metal pool from the cathode and the bath freeze re-dissolved. Analyses of this bath freeze indicated that it was cryolite/chiolite material, a ratio of the cell bath of aluminum fluoride and sodium fluoride that is solid at the 780 degree C operating temperature range of the low temperature cell. Current efficiency for the 100-hour run was 81+%. The current efficiency was reduced by parasitic currents created once the cathode was raised to break direct electrical contact with the metal pad and the problem of continued metal burning on the cathode riser at the bath surface.

Following the 100-hour run on August 21, the next run was set up as a 100-hour run in a similar fashion and performed starting on September 4, 2001. This run was operated with the cathode electrically disconnected from the metal pad and no bath freeze on the metal pad was experienced. The current efficiency for this run was 83%; again it was reduced due to the parasitic currents from the anode through the metal pad to the cathode. Attempts were made on this run to fasten alumina blocks on the cathode risers at the bath line to prevent the surface tension of the aluminum metal from drawing it to the bath surface where there was re-burning. During the run, these blocks cracked off of the cathode riser and the latter

part of the run still experienced metal burning at the bath line on the cathode risers.

After the two 100-hour runs, a short run was performed to test alternate methods of protecting the anode and cathode risers at the bath line. Prior analyses had indicated that the bath line where the anode riser penetrates the bath was an area of accelerated anode corrosion and on the cathode, the metal-wetted cathode riser was a production efficiency loss due to re-burning the metal at the bath interface.

The next run performed on September 26, 2001 was a 49-hour run to test revised anode and cathode riser protection as well as revisit the double-crucible concept to drain the metal from the primary container into an outer container to avoid parasitic current. In this test, the inner container did not have a bottom anode. This test recorded a current efficiency of 93.5% for the duration of the run and demonstrated that the parasitic current losses could be greatly reduced while still leaving the metal pad electrically isolated from the cathode to avoid bath freeze. The high current efficiency showed that protection of the cathode riser at the bath line could eliminate the efficiency losses due to metal re-burning in the surface foam of the bath.

In mid-2001, the decision was made to relocate the development activity to a larger development line to be located at The Dalles plant. The three-man crew at the pilot plant performed conceptual engineering for the development line and an outside engineering firm was contracted to perform the detailed design and monitor construction. The planned date for relocation to the enlarged facility was at the end of the year, 2001. With the time approaching for dismantling the pilot plant at Goldendale, the last three major runs were planned to put all of the experience gained at that facility to use.

Analyses of the prior operations of the inert anode cells had demonstrated that with low current densities and short anode-cathode distances (ACD), the inert anode cell could run at a voltage of 3.2 volts compared to the nominal 4.0 volts of a new, modern conventional cell. The other potential savings of inert anode technology of the material and manufacturing cost of continuous replacement carbon anodes would be partially offset by the increased cell construction cost of utilizing TiB_2 or other exotic materials for the cathode. Examination of the data produced indicated that the inert

anode cell was not particularly sensitive to the electrical current load. Successful runs had been performed at current densities as low as 0.25 amps/cm² and as high as 1.0 amps/cm². This led to the conclusion that, in addition to energy savings, an inert anode cell could potentially save energy costs by using time-of-day electricity that on a thermal power system could be as much as three times lower in cost in non-peak periods as during high demand periods.

The next major run was a 100-hour run performed commencing October 23, 2001, and was set up as a test and demonstration of the dynamic range of an inert anode cell. It was a single-container run without a bottom anode but with provisions for draining the metal pad behind an anode to reduce parasitic current. The run was operated at a current density of 0.5 amps/cm² of cathode area for the first 24 hours, then moved up in fairly rapid order to a density of 0.85 amps/cm², then to 0.9 amps/cm² and operated at this range for 48 hours, then reduced back to the 0.5 amps/cm² for the remaining 28 hours of the run. This sequence was to approximate an inert anode cell operating at low current load during a high-cost power period, increasing to nearly double the current load for a weekend where power costs could be low, then returning to low power mode following the weekend. This run was at a cell voltage of 3.2 volts at the end of the first 24 hours operation, the voltage increased to the range of 3.8 to 3.85 volts during the high current period, and then reduced to 3.2 volts during the last quarter of the run for the second low power period. This run demonstrated that the inert anode cell has the potential to not only run at lower electrical usage than conventional technology but also to utilize lower-cost interruptible and short-term available power.

Run charts from this run are included later in this report.

Following this run, the next major run was set up as an alumina double-crucible run with a bottom anode in the inner crucible. The purpose of this run was to prove that an active bottom inert anode cell could be fabricated that would allow metal to be drained out the bottom of the inner container and tapped by conventional means. This run was for 96 hours duration and terminated when the titanium diboride cathode riser broke. This run was operated at a current density on the cathode of a nominal 0.75 amps/cm². The overall current efficiency of the run was only 82.5%. Difficulty was experienced early in the run with cathode wetting, which required removal and scraping of the cathode assembly. Also in the first

half of the run, the cathode assembly was not submerged as deeply below the bath as planned and there was some metal burning due to exposure of the cathode edge to the oxygen foam on top of the cell. This was eventually realized and during the latter part of the run, current efficiency was estimated at 90+% based on tapping quantity. This run was significant in that it demonstrated the produced aluminum could be drained through a hole in an active anode bottom without difficulty even if the cathode assembly was not precisely located with respect to the bottom anode hole. It verified the engineering calculations that a liquid conductor in a self-created magnetic field would align itself with the center of the hole. At the moment the metal droplet became too heavy to remain on the cathode by surface tension and broke direct contact, a surge of current occurred due to the momentary elimination of the decomposition back potential. This had the effect of centering the metal drop in the hole of the bottom anode and propelling it through that opening. Again, as in the prior run, the data from this run indicated the stability of the Cu-Ni-Fe anodes in that the voltage for the last two days of the run was steady and slightly declining.

Run charts from this run are included later in the report.

Following this run, on November 26, 2001 a 136-hour double-crucible run was performed re-utilizing the same anodes without cleaning or modification. This run was terminated when the local public utility district had a power failure at 11 PM on the sixth day of the run. During this run, a portion of the supplemental heaters for the cell failed and the desired operating temperature could not be maintained at a stable value due to bath sampling and metal tapping disruptions. The cell was operated at higher than planned current density to maintain heat. Also during the run, the alumina sleeves protecting the anode risers from corrosion at the bath line cracked and partially plugged the hole in the inner crucible and difficulty was experienced in getting the metal to drain to the outer crucible for tapping. The lesson from this run was that although the riser protection sleeves may appear intact at the completion of a run, the infiltration of bath into the insulation reduced the flexibility of the protective sleeves and that the sleeves could not be reheated without the risk of breakage.

Pilot plant dismantling for relocation to The Dalles commenced in December 2001. One final short run was performed at the pilot plant to test the effect of calcium fluoride in the bath of the inert anode cell. Some of the results of examination of anode blisters (excessive corrosion) reported to

the Seattle laboratory had raised the concern that any calcium in the bath might create this destructive corrosion of the anodes. Analyses of the baths from the several extended runs at the pilot plant utilizing smelter-grade ore, which contains a small amount of calcium as an impurity, indicated that the pilot plant had exceeded the maximum calculated level of calcium without experiencing the potential difficulty. A one-day run was set up with calcium fluoride deliberately added to the bath to approximate the steady-state ratio of calcium in a continuously operating cell using smelter grade ore. This run was performed and indicated that calcium fluoride in 1% or greater concentration did not create unusual anode corrosion.

Phase 3 - Personnel training and metal quality:

Up through Phase 2 of the development activity, no significant attention had been paid to metal quality of metal produced during the development activity as physical and tapping solutions were addressed. A good part of the activity at the pilot plant had utilized titanium cathodes that continuously alloyed with the produced metal. Tapping had been performed with stainless steel spoons that were partially dissolved over time by the liquid aluminum and that also contributed to contamination. Ordinary tools had been used for cell examination and the ore feed/fume-scrubbing ducting was constructed of copper tubing. Upon relocation to the new development facility at Northwest Aluminum in The Dalles, Oregon, the following new tasks were addressed:

- Relocate sufficient capable personnel from the smelter workforce and train them in the new technology,
- Assume responsibility for additional testing of copper-nickel-iron anode compositions,
- Prove that high quality aluminum could be produced utilizing metal anodes and smelter-grade raw materials,
- Design, construct, and commission a 5,000-ampere pilot cell.

At The Dalles, additional personnel were added to the development crew to expand from the original three persons to a total of ten. This was to allow the longer test runs to be performed in a more rapid sequence while at the same time free up the original personnel for design and fabrication of the next generation of development cells up to 5,000 amperes.

The Seattle Laboratory testing in the 10-ampere cell was an arrangement where the only anode was on the bottom of the cell and a single cathode was suspended above. In the 200-amp cell, the Seattle laboratory's tests had all been performed with a cast alloy active anodic container and anodes of the same alloy. This necessitated the casting of the difficult and expensive alloy container along with casting and fabrication of the anode plates. At Goldendale, the pilot plant developed a procedure of using purchased high-density alumina containers, which allowed test runs to be rapidly configured since only simple, inexpensive anode plates were required. The container added no contamination to the cell, and a new container could be used for each test run to avoid cross-contamination from run to run without excessive expense. It was concluded that these procedures would allow the testing of additional anode alloys in a configuration more closely matching the planned commercial cell without the expense associated with preparing both container and anodes of the same alloy.

New run ovens for the development line 200-amp cells were constructed and additional metering and monitoring equipment was installed. An X-ray fluorescent unit was procured and installed to allow monitoring of bath composition and metal quality while runs were underway instead of obtaining the results two to three weeks after the completion of a run. As the additional personnel were added, eight demonstration runs were performed to commission the new equipment and train the incoming personnel. The individual previously in The Dalles Metallurgy Department, (who had been responsible for fabrication of the pilot plant anodes up to that time) was added to the development line crew and the development line assumed all responsibility for the casting and fabrication of the anode alloys to be tested.

Based on the experiences gained in the Goldendale pilot plant, the standard 200-amp cell test for anode alloys was designed to be a single alumina crucible, smelter-grade sandy alumina, smelter-grade raw materials, 1% calcium fluoride in the bath to approximate steady-state conditions, and metal collection in the bottom of the cell. The removal of metal was with molybdenum tapping ladles, since molybdenum was not a significant contaminant in any of the raw materials. The standard test run was determined to be 72 hours, based on results from the Goldendale pilot plant that indicated the cells achieved stability prior to that amount of time. The testing sequence was that two cells would be run simultaneously for a test run during one week, then two new setups would be fabricated and as

sembled the following week for another two-cell run in the third week. Cell upheal would be performed on Monday of the run week, cell startup Tuesday morning, and the cell would be operated at the test program conditions for three full days. After the third day and collection of the 72-hour metal tap, additional tests at higher or lower current, increased or reduced temperatures, and modifications to bath or feed, could be performed for the fourth day of the week. By running simultaneous tests of under the same operating conditions, the performance of different alloys could be examined and compared under the exact same operating conditions or the performance of a single alloy could be directly compared under different operating conditions.

An initial wide range of alloys of copper-nickel-iron was proposed for testing. Also tests were run on pure iron and pure nickel. All total, 46 runs of the nominal 200-amp cell were performed in the anode testing program. Some tests were also performed with bath compositions that included the substitution of a significant percentage of sodium fluoride with potassium fluoride. Most of the test runs were for 72 to 100 hours or more hours except for a few early failures. Higher temperatures than the 800 degrees C maximum used at the Goldendale pilot plant were also tested, and some runs were made up to a maximum temperature of 840 degrees. Most of the tests were performed with an ACD of 0.75 inches (to make the cell less sensitive to assembly) and at a current density of 0.75 amps/cm^2 (mid-point of the projected dynamic range of 0.5 to 1.0 amps/cm^2).

Each run was started with all new bath materials and new alumina containers to avoid carrying anode metals or cathode metals from one run to the next via the bath. All tests were performed with hot-pressed TiB_2 cathodes of various thicknesses. Since the bath composition for each run was new and smelter-grade raw materials were used, silicon was a common contaminant of the produced metal, as smelter-grade aluminum fluoride is high in silica contamination. In conventional smelter operations, the amount of aluminum fluoride added to a continuously operating cell on a daily basis is small and silicon from this source is at an acceptable level in conventional smelting. Although reagent-grade bath materials could have been used, this would result in additional expense and would void the requirement that development be with conventional materials. As a result of this, the first metal removed from the inert anode cells was high in silicon. This level declined throughout the duration of most of the runs, although bath replenishment was necessary during the runs to replace bath mate

rial lost during tapping and bath extracted on a regular basis for in-run analyses, which over the duration of a run, was fairly significant on these small cells. For purposes of metal quality evaluation, silicon was ignored since it was not a component of the anodes, cathodes, or cell containers and is a known quantity in the aluminum fluoride that results in 0.02% to 0.04% metal contamination in conventional cells.

With respect to metals in the anodes and cathode, by mid-2002, metal quality of 98.5% or better was achieved using metal anodes of copper-nickel-iron composition. This quality number also included any titanium in the metal that was presumed to come from any deterioration of the TiB_2 cathode, although titanium is also a potential contaminant in smelter-grade alumina. The iron included in the contamination of metal quality was both from the iron component of anode alloy as well as iron in smelter grade alumina, which contributes at least 0.02% to the metal. By the early fall of 2002, metal quality of 99.5% was achieved in the standard test cell with standard components (again, ignoring silicon) at the 72-hour benchmark. Also by the early fall of 2002, runs of up to 172 hours had been performed.

Graphs of metal quality progression in 2002 are included in a subsequent section of this report.

In early 2003, some tests were performed with modified baths where 50% to 75% of the sodium fluoride was replaced with potassium fluoride. These tests generally would have better metal quality and a slightly lower operating voltage on the same anode composition than the standard NaF-AlF_3 bath. Some very interesting results in both metal quality and cell resistance control were achieved with potassium-modified baths, but these were not investigated in detail since at this time, the expense of potassium fluoride is much greater than sodium fluoride so it is not as practical for commercial operation. In addition, the production of smelter-grade alumina by the Bayer process results in a continuous small amount of sodium in the ore, so maintaining the given ratio of potassium in a continuously operating commercial cell would require bath replacement on a continuing schedule.

Runs with potassium-based baths showed more dissolution of the alumina container and the alumina protective sleeves over the anode and cathode risers and, under identical operating conditions, resulted in lower current

efficiencies by approximately 5%. The metal quality graph from one of the potassium-based bath runs is shown in the subsequent section.

By mid-to-late 2003, tests of duration of up to 320 hours were run and current efficiencies in some of these extended tests were in excess of 95%.

In many of the tests, with two cells operating simultaneously, comparative tests were performed, where one cell was be operated at 830 degrees for example while the identical alloy and setup in the other cell was operated at 780 degrees. On many of the 100-hour or greater runs, after the 72-hour bench mark, significant changes in temperature or current density would be made to evaluate the results compared to the same cell just prior to the 72-hour bench mark.

Tests were performed with the same anode alloy but with physical modifications, such as homogenization after casting versus non-homogenized. A few tests were run with anode material of copper-nickel-iron composition that had been vacuum-cast and hot rolled. This test series was limited due to the difficulty experienced in obtaining small quantities of hot-rolled plate of this difficult alloy to roll. This limited testing did not demonstrate any particular advantage to hot-rolled plates versus cast plates. Only a few tests were performed with a double-crucible setup and an active bottom anode due to the additional time and expense of constructing this type of assembly. To some degree, each run was unique and not necessarily identical in results to an identical setup run at a different time. General patterns were developed leading to a greatly narrowed preferred range of copper-nickel-iron alloys and the relative effects of each element on cell resistance, metal quality, and voltage stability were determined.

As economic conditions for the industry worsened and additional research and development funds were curtailed, this program was reduced in late 2003. The ideal anode alloy has yet to be determined, but the results achieved indicate that there is a high probability of an alloy composition and physical treatment that will give a successful long-term stable anode for the inert anode cell. These results also provided an indication of the range of alloy compositions to achieve this result. Late in the program, an additional element was added to the anode composition that resulted in improved metal quality, more stable resistance and lower voltage. When further anode testing is resumed, anodes with this element and corre

sponding changes in the percentages of the other anode components should prove very interesting.

Phase 4 -Design, construct and operate larger cells:

The overall reason for the establishment of inert anode development activities at one of the smelters was to design and operate an inert anode cell of 5,000 amperes capacity. Design on this phase of the development process commenced in mid-2001 at the Goldendale pilot plant prior to any successful run of the 300-amp capacity cell in excess of eight continuous hours and prior to resolution of the planned methods for tapping the cell. Aside from the selection of anode material, development of a tapping method, and resolution of the method of fabricating an anodic container of sufficient size, there were a number of other issues to be resolved in the construction of a larger cell. Many of these could not be tested in the small-scale of the 300-ampere cell and the conclusion was reached that in order to learn how to build a 5,000 ampere cell, one would have to be built.

A rectifier capable of operating up to four 5,000-amp cells in series was ordered and delivered in 2001. Estimates were made for the physical dimensions and weight of a 5,000-ampere cell in order to size the development line dimensions and capacities of the intended overhead cranes. The development facility at The Dalles was constructed in late 2001 for occupancy in early 2002. Included within the design of this facility were two overhead cranes and a separately filtered and ventilated rectifier room. Space was reserved for bath melting, cell internal preheating, metal tapping, and for shop equipment necessary to fabricate, assemble and repair the planned cells. Computer monitoring and control equipment for the 5,000-amp cell was selected and portions of this equipment procured and utilized in the 300-amp cell at the Goldendale pilot plant.

With the additional personnel trained and continuing the testing program for anode alloys, efforts were concentrated on the design and construction of the 5,000-ampere cell. Based on the late 2001 runs at the Goldendale pilot plant, it was decided that the elements of the 5,000-ampere cell should include:

1. The ability to test the dynamic operating ranges from 0.5 to 1.0 amperes/cm², or a current range of 2,500 amperes to 5,000 amperes.

2. A minimum bath quantity per ampere determined by the 200 amp testing at Goldendale.
3. An active bottom anode or provisions for installation of one.
4. An integral dry scrubber using the ore feed to the cell to scrub the off-gas from the cell.
5. The ability to tap by conventional means, either vacuum tapping or ladling out of the bottom of the cell.
6. A steel outer container lined with alumina castable refractory. This would not be externally heated, if supplemental heat was required, it would be internal to the outer steel container.
7. All active internal components (anodes, cathodes and electrical connections to them) suspended from the cell top or lid to avoid penetration of the alumina lining below the bath line.
8. A cooling system for the alumina castable refractory such that there would always be a point within the thickness of the lining that was at a lower temperature than the lowest melting point of the cell bath and metal.

Based on the planned current and the current densities desired, the anode and cathode areas were determined. The number of cathodes was dictated by the largest available size of commercial hot-pressed TiB_2 plates (nominal 16 inches by 16 inches) and the physical volume of the cell was dictated by the requirement to maintain a minimum grams of bath per ampere at the highest expected load. Once the cathode size and number was determined, orders were placed for cathode plates of the necessary size. The arrangement and size of the anode plates was dictated by the cathode selection and work was commenced on finding a source for anode plates of this size and arrangement. The bath volume and the available TiB_2 plate sizing confirmed that the electrical connections to the cathode would have to be made at or below the bath line within the cell.

An electrical connection technique consisting of a molybdenum riser bolted to a tab on the TiB_2 cathode and treated to provide a solid, low-resistance joint was devised. This connection was designed to be contained within the alumina sleeve and castable that provided protection for the cathode riser at the bath line. Examinations from the 200-amp runs had shown some creeping of liquid aluminum up the TiB_2 risers within the alumina castable protective sleeves, so a method was devised to provide a metal stop within the protective sleeves so that liquid aluminum could not impact on the molybdenum-to- TiB_2 joints.

This technique and the materials involved were tested in two of the 200-amp runs in the development line and proved electrically robust over the duration of 100-hour runs.

In order to achieve an active bottom anode, a novel approach to the double-crucible design was invented. The anodes were assembled inside of a metal box constructed of anode alloy material and this box submerged in the bath contained within the alumina-refractory cell lining. The bottom of the anode metal box had drain holes located below corresponding metal drain tips on the cathodes and as metal was produced on the cathodes, droplets would form and fall through the bottom anode drains into a metal reservoir underneath the anode box. Tapping would be by ladle or siphon from a tapping well within the outer liner but external to the anode box. Although the metal produced would be at anode potential beneath the anode box, the bottom anode shielded it from a clear current path to the cathodes and therefore parasitic currents were nearly eliminated. The construction of the anode box required welding of the anode alloy materials. The box was designed so that none of the welds were under tension and since the box was submerged in the bath and with holes in the bottom, it was not necessary that the welds be leak-proof.

A photograph of the completed anode assembly is shown in a subsequent section of this report.

The TiB_2 cathode plates were individually suspended by the molybdenum risers between the anode plates welded to the sides and bottom of the anode box. To control the flow pattern and circulate fresh alumina to the active components at all times, two anodes were used for each cathode and space was provided between adjacent anodes to allow enriched bath to flow downward and across the bottom anode and up through the active zone between the anode and cathode. Due to the lift provided by the oxygen foam from the active sides of the anodes, there would also be upward flow through the holes in the bottom anode beneath the cathode drain tips, so provisions were incorporated to provide some flow of alumina enriched bath over and through one end of the anode box. Based on experience gained from the 200-amp cell runs with a double crucible and active bottom anode, this upward flow through the metal drain holes would not result in a problem of metal draining through the holes.

Difficulty was experienced in locating a foundry to cast anode plates of the size required. Large foundries that may have the technical capability and resources to cast these materials were not interested in a job involving only a few hundred pounds of casting. Small, local foundries that were interested in doing this work did not have the technical resources. Several attempts were made to cast the nominal 24" by 24" anode plates at foundries in the NW and the smelter metallurgical department worked directly with these outside vendors without success. An East Coast specialty firm agreed to attempt to vacuum cast and hot roll the materials necessary for two 5,000-ampere cell anodes, but in the final analysis, was able to produce only half of the plates required for one cell. It was concluded that if anodes were to be obtained for the 5,000-amp cell, they would have to be fabricated by the development line itself. Without the capability to do hot or cold forming of plates in the dimensions necessary, it was decided that the plates would be cast and machined to final thickness after casting. Eventually, the development line cast the necessary anode materials utilizing heated graphite molds with controlled cooling. Anode plates were machined and shaped in the small machine shop constructed as part of the development line. A procedure for TIG welding the anode alloy was developed that was satisfactory for the purposes of assembling the anode box and making the required electrical connections.

The requirement to always have a bath freeze zone inside of the primary alumina lining of the cell required that the cell lining have cooling tubes buried within the cell near the exterior of the alumina lining. The steel shell of the cell remained cool by incorporating the necessary thickness of high thermal resistance castable insulating refractory between the alumina lining and the steel shell. The plans for operation of the 5,000 ampere cell included operation at currents as low as 2,500 amps to verify the dynamic range was sufficient to allow significant time-of-day power variations. Preliminary calculations indicated that at currents below 4,000 amperes, there would be insufficient heat to maintain the desired cell temperature without supplemental heating. Refractory-sheathed heaters were designed and installed in troughs in the bottom of the alumina lining such that the troughs would always remain filled with aluminum metal and protect the heater sheaths from the bath.

The anode box and cathodes for the cell were suspended from their respective electrical busbars mounted on the lid of the cell. The lid and assembled anodes and cathodes were preheated in an inert atmosphere to

avoid oxidation of the cathodes and to raise the cathode plates at an even and controlled rate to avoid thermal shock. A commercial ceramics kiln was ordered and modified to provide for argon shielding and upheal of the internal assembly while mounted to the cell lid.

One of the bigger design issues was how to mount the cathode risers to the cathode bus. For support and electrical connection, two cathode risers on each cathode plate were required. Due to the fragile nature of the TiB_2 cathode plates, any side stresses on the cathode tabs had to be avoided. On the other hand, to maintain the tight ACD some 24 inches away from the cathode support bus required that the positioning of the cathode plates between the anode plates be precise and rigid. The design eventually evolved to two pin connections at the cathode bus for each cathode riser and an electrical flex to the riser from the bus. The pins would precisely align the cathode plate in the vertical direction and in the horizontal direction of the ACD, but allow flexibility in the third direction to avoid side stress (wishbone) on the cathode tabs. Some clearance between the cathode risers and the holes in the lid was incorporated in the design to allow for thermal expansion during upheal of the internal assembly. Since the cell lid (and anodes) in the cell would expand at a different rate than the cathode and the buses outside of the cell, during upheal in the clearance was monitored. Once the assembly was installed on the cell, it was predicted that the bath vapors would condense around these openings after a couple of days of operation and eliminate the designed clearance. Since the cell temperature was to be controlled within a fairly narrow range, it was expected that there would not be significant differential thermal expansion once these openings were sealed, so the cathode tabs would not be under undue stress.

The final design issue was how to melt the approximately 250 kilograms of bath required for the cell. It was decided that since the cell would have supplemental heaters in the bottom, the size of these heaters would be increased and used to preheat the cell lining and melt the starting bath powders. To avoid bath attack on the heater sheaths, the heaters would have to be submerged in molten metal before the bath started melting. To avoid thermal shock on the heaters and to season the cell refractory castable, the upheal would have to be at a slow and controlled rate. It was therefore decided to place aluminum metal bars alongside and above the heater troughs in the bottom of the cell. The plan was for the metal to melt before the melting temperature of the bath materials was reached.

Since aluminum fluoride is denser than liquid aluminum, the heater troughs would have to be protected until the bath materials melted and became less dense than the liquid metal. The heaters troughs were installed in alumina sleeves in such a manner that liquid metal could fill the sleeves but solids such as the bath powders would be excluded. The bath powders were placed in an aluminum box that would contain them until the temperature of the box bottom reached its melting point. It was estimated that some sintering of the NaF and AlF_3 particles would occur by that time and that some liquid bath would form nearly immediately.

Although ordered in mid-2002, cathode plate materials were not received until late April 2003. The hot-rolled anode materials from the specialty metals firm on the East Coast were due in February 2003, but none were received until May 2003 and then not a sufficient quantity to construct even one anode assembly. All priority was given to in-house casting and machining of anode plates to fabricate the first two anode assemblies for the first 5,000-amp cell. A local outside shop fabricated the potshell and cooling tubes as an assembly. The development line installed insulating castable, the castable alumina lining, and the bottom supplemental heaters. As anode assemblies were cast and machined, they were welded into the anode box for the first cell construction. Cathode risers were fabricated in house. The TiB_2 cathode plates were machined to provide the drain tips and tabs by a local EDM shop and then assembled to the electrical risers by the development line.

Upheat for the first run of the 5,000-amp cell was commenced on June 25, 2003. The temperature of the internal heaters was ramped up to their maximum rating of 1,000 degrees C. Without initial submersion in molten metal, the output of the heaters could only achieve approximately 20% of their full power rating and this was insufficient to perform the desired cell upheat and bath melting. The alumina shielding above the heaters combined with the high heat transfer rate of the solid aluminum above the shielding prevented temperatures in the cell from reaching those necessary to melt the metal and provide submersion of the heaters to achieve their full power. Eventually, a gas-fired indirect heating tube was inserted into the bath powders and bath melting started from the top. At some point during the cell upheat, the liquid bath reached the bottom of the aluminum metal box, the aluminum melted and flushed liquid bath down into the heater troughs. Although this did not cause failure of the heaters, it limited the heater output to about 40% of the design and continued to cre

ate problems in reaching the desired cell temperature. When the temperature was finally reached, the preheated internals were inserted and power applied to the cell and raised to 4,000 amps in fairly rapid increments. For several hours after startup, cell temperature continued to drop and the cell was operated at very low relative temperatures. To assist in increasing bath temperature, insulation was added to the cell lid and around the anode and cathode risers after the cell had been in operation approximately 16 hours.

The cell was energized on July 3 and operated for approximately 40 hours before the run was terminated. Analyses after termination revealed that the initial charge of solid metal bars in the bottom of the cell had never melted and that there was still a layer of non-melted bath powders in the bottom of the cell. Liquid metal had drained down into the heater troughs, but also bath and bath powders were in the heater troughs and the heaters were effectively insulated from being able to achieve the designed power output. The bottom of the anode box was essentially setting on bath powders and the metal reservoir was filled with non-melted metal bars and bath powders, preventing metal produced on the cathodes from draining into the reservoir. In the first 16 hours of low temperature operation, bath vapors had frozen around the cathode risers exiting from the cell lid and eliminated the thermal expansion clearance that had been expected to last until a stable temperature was reached. The addition of insulation to the exterior of the cell lid after that time to assist in increasing cell temperature had resulted in differential expansion of the lid after this clearance was eliminated. The resulting stress had broken two of the six cathode risers, although this was not apparent during operation of the cell as all cathodes remained energized.

To remove the metal and bath from around the heaters in the bottom of the cell would have required a time-consuming removal and replacement of the cell lining. With this phase of development already behind schedule, it was decided to modify the second anode assembly to remove the bottom of the box and make a 5,000-amp cell run as a single-container setup. Additional gas-fired indirect heaters were fabricated to speed up-heat. The second internal assembly was modified to eliminate the box bottom and to raise the anode and cathode assemblies to provide more room in the bottom of the cell and reduce parasitic currents. Additional clearance was also designed around the cathode riser penetration through the cell lid and flexible fume shielding was designed around these larger

openings. Upheat for the second run commenced on July 23 and electrolysis commenced on July 25. The cell was operated for approximately 80 hours at currents between 4,000 and 5,000 amps before being shut down due to obvious internal problems. Although over 100 pounds of metal was produced and tapped from the cell, the cell still suffered from low temperatures in the bottom and the supplemental heaters still did not achieve but about 40% of their design capacity.

It was decided not to perform additional 5,000-ampere runs until an external bath melter could be designed and procured to allow a hot start for the cell; until alternate arrangements were developed for the supplemental heaters to get full output; and until a method of draining the produced metal completely away from underneath the internal anode assembly was designed. These steps would require a complete rebuild of the cell. Analyses of the results of the two runs of the 5,000-ampere cell also indicated that the liner cooling system required redesign to more evenly remove the heat from the cell lining. The original system of imbedded air tubes resulted in some areas of the lining (where the air entered the tubes) being too cold while other areas of the lining were at temperatures approaching the melting point of the bath and dictated that more cooling air needed to be added.

To develop these new design concepts, an intermediate cell of a maximum of 1,000-ampere capacity was constructed. The first cell of this size was designed as a heavily insulated steel box with an internal high-alumina refractory lining. Supplemental heat was necessary for all levels of operation of this cell. The heaters were designed to suspend vertically from the lid of the cell with refractory-filled alumina sleeve protection from the cell lid to below the bath line and graphite sleeves below the bath line to allow better heat transfer and protect the heater sheaths from bath and liquid metal. A single large cathode of TiB_2 was sandwiched between two anode plates. The bottom of the cathode was sloped to a drain tip on one end. The two anode plates were joined across the bottom by a bottom anode plate following the slope of the cathode but slightly shorter so as to not interfere with metal draining off of the lower end of the cathode. The metal reservoir was at the cathode drain end of the assembly and all accessible from the tapping well with no portion underneath the bottom anode yet drained away from the cathode in such a fashion as to avoid parasitic currents.

The design of this cell was such that it represented a module of a 5,000-ampere cell should the design prove successful. This cell was constructed and operated in late September 2003. The cell was operated for 130 hours and shut down when the TiB_2 riser tab on the cathode failed. The cell was initially tapped at 12-hour intervals and then tapping was reduced to 8-hour intervals to better judge current efficiency and quality. Except for the first three taps, current efficiency was very high at 94% to 95% on all subsequent taps. Overall current efficiency for the 130-hour run was 92.5%. Anodes for this run were from the vacuum cast hot rolled plate material originally intended for the 5,000-ampere cell. Initial metal quality was reasonable for startup but later in the run deteriorated. The cell still suffered from thermal distribution problems with a colder than desired bottom temperature in the cell. The cell was operated at a steady 900 amperes representing 0.9 amps/cm^2 current density on the cathode. The bath for this run was composed of sodium fluoride and aluminum fluoride with no calcium additive. Regular bath sampling at 8-hour intervals indicated that the bath gained calcium at a much higher rate than the calcium level in the ore and at the end of the run, calcium in the bath represented 1.3% of the bath weight.

Analyses at the end of this run indicated the following:

- The cathode tab failure was due to de-lamination of the hot-pressed TiB_2 plate. This type of failure had occasionally been experienced with the 200-amp cathodes and almost all prior TiB_2 cathodes had shown a tendency to delaminate. The likely cause of this is impurities and imperfections introduced during the hot-press sintering process.
- The metal quality problem was increased corrosion on the inactive sides of the anodes. The anodes did not have the perforations normally used in the 200-ampere tests to provide some activity on the backsides.
- The graphite sheaths of the supplemental heaters would not have lasted for the planned 500 hours run duration. Although protective of the heaters in the bath, the graphite was conductive and provided a slight parasitic current path from the metal anodes to the cathode with the net result that the graphite was anodic. As anodes, some oxygen was produced on the heater sheaths and slowly burning away the graphite. The high-density alumina outer sheaths of the anode risers, the cathode riser, and the supplemental heaters showed some dissolution and likely would not have lasted the duration of a 500-hour run.

- The source of the calcium was the high-alumina refractory of the inner cell lining. This refractory was 3.2% calcium by weight. Although the calcium in the bath did not appear to affect the cell operation, the loss of calcium raises concerns regarding the longevity of the high alumina castable as a cell liner.
- There was still an unfavorable temperature distribution within the cell. The cell was operated with an upper bath temperature higher than planned to maintain a reasonable temperature in the bottom of the cell.

At the completion of this run, the development line crewing was reduced in half due to continuing poor economic conditions for aluminum smelters in the Northwest and the layoffs affecting both the Goldendale and Northwest Aluminum smelters.

A second and final nominal 1,000-amp cell was constructed and operated to test potential ways of stabilizing the temperature distribution and to address the continued weakness of the TiB_2 riser tabs. As this was clearly to be the final attempt before hibernation of the development line until better economic times, radical design changes were made for this test. The same heavily insulated outer shell from the first 1,000-ampere cell was re-used, but the high alumina castable liner was formed inside of a heavy-walled copper box that was placed in the insulated cell. The anode risers were run horizontal and connected to the copper box by penetrating the alumina lining. A layer of sodium fluoride was cast between the copper box and alumina lining at the anode risers to create a chemical freeze zone should bath leak along any seams between the anode risers and the alumina liner. The cathode riser was similarly configured to penetrate the alumina liner horizontally, again with a chemical freeze layer as well as a metal stop layer of silicon carbide to prevent liquid aluminum from wicking along the cathode riser. The TiB_2 tab on the cathode riser was made much wider to add strength in case of continued delamination. Supplemental heat was supplied to the cell by heaters on the bottom exterior of the copper box, with the copper to act as a heat sink to provide even top to bottom heating. The anode bus was connected by welding copper conductors to the copper box and exiting out the top of the cell to the anode bus, so that the copper box was at anode potential. The arrangement of the anodes with respect to the cathode and metal tapping well was similar to the first 1,000-amp cell design. This overall design could not function as a module of a larger cell.

This final run was operated for approximately 60 hours. The run was terminated due to excessive corrosion of the anodes at the cathode riser end of the cell. Examination at the conclusion of the run indicated that the alumina lining around the cathode riser had failed, allowing the semi-conductive silicon carbide metal stop refractory material behind the lining to slough into the cell. This provided a path for conduction from the cathode to the anodes and the production of liquid aluminum in contact with the anodes that destroyed the metal oxide coatings.

Analyses of this run indicated that the heavy copper intermediate shell provided reasonably good thermal distribution. The run was too short to evaluate the possible function of the chemical bath freeze at the anode risers. The welding of the anode risers to the backs of the anodes was in good shape and indicated that the anode welding techniques developed during the 5,000-amp and 1,000-amp cell constructions were suitable for electrical connections and reasonable structural support.

Shortly following these last runs, the development effort was reduced to one full time and one part-time person performing analyses of the development activities and researching improved materials for use when activities resume. Most of the key individuals associated with the development activity were relocated to security and maintenance activities within the two closed smelters so that they will be readily available when development resumes.

Arrangement of Equipment and Adopted Procedures:

Goldendale Pilot Plant 300-amp cell:

The first 300-amp cell tests at the Goldendale pilot plant were performed utilizing a 60Cu-25Ni-15Fe cast container provided by the Seattle laboratory. Two ovens were constructed utilizing an electric ceramic heater on the bottom and electric radiant heaters on all four sides. The tops of the ovens were fabricated from a two-inch thick insulating refractory board with a cutout to match the cast container top dimensions. The design principle of the ovens were that the bottom heaters would be used to control cell temperatures while the radiant side heaters would be basically set to the desired cell temperature and function as lossless insulation for the cell. The top of the cell container was spaced into the lid by cast iron plates placed on top of the bottom heater with the container setting on the

plates. After a couple of early runs, it became apparent that some of the bath vapors condensed to liquid at the top of the cast container and drained down the outside and over the edge of the cast iron plate on top of the bottom heater. This resulted in damage to the heater as the bath liquids dissolved the refractory base.

To compensate for this leakage, the oven setup was revised by purchasing a cast iron skillet and placing it on top of the cast iron plates and, once the cell container was placed in the skillet, putting approximately $\frac{1}{2}$ inch of alumina in the skillet around the container.

Within the rectangular metal container, the cathode assembly and an internal anode were suspended from the lid of the oven. The cathode assembly for the first series of runs at the Goldendale pilot plant was constructed of titanium metal. Two nearly square boxes were formed of titanium with a titanium rod at each corner exiting a stainless steel lid for the cell, resulting in eight cathode risers for the electrical connections. The titanium cathode risers were protected with alumina tubes extending from outside the cell to below the bath line to protect the titanium from corrosion. The boxes were positioned so that three sides of each box were at the desired ACD (in these runs typically $\frac{1}{2}$ inch) from the sides of the cell container. Between the two cathode boxes, a single anode plate was positioned at the same ACD from each box so that the fourth side of each cathode box was also opposite an anode. In this arrangement, bath flow was upward on all four sides of the cathode boxes and downward on the inside of the boxes and only the outsides of the cathodes were active. Alumina feed was positioned over the upwelling from the center anode.

The cathodes were powered from a copper bus attached to the lid of the cell, which was cathodic. The cell container extended partially into the two inches of refractory board forming the top of the oven. The center anode was powered with a copper flex connected to the same tab that protruded down into the oven to power the cell container as an anode.

The startup of a cell was accomplished by placing the cell container in one of the ovens and filling it with the NaF and AlF_3 powders in the correct ratio to melt to a eutectic bath. The container was then covered with insulation and heated to melt the bath components. Once melted, additional NaF and AlF_3 were added in powder form to bring the bath level to the desired height of approximately one-inch below the top of the container. The

bath was heated to a temperature of 800 degrees C or hotter prior to startup. This procedure took approximately three hours. In the second oven, the internals (the cathode boxes assembled along with the internal anode) were preheated to approximately 700 to 750 degrees C. The rectifier cabling was connected to the cathodes and to the run container and energized at a current set point with a voltage limit. For most of the test runs, this current setting was the full current (300 amperes) planned for the run. The voltage limit was set to a value sufficient to produce metal but low enough so that if the cathodes or anode initially experienced high resistance, no area of the cell should experience excessive current. This value was generally in the range of 3 to 3.5 volts.

When the cathode internals were inserted in the cell, electrolysis began immediately and once the cell had stabilized and was at the desired operating temperature, the clamp on voltage was raised to achieve the full current if the cell was not already at that value.

After some number of runs, the preheating of the internals was often discontinued and the internal assembly was inserted cold with immediate electrolysis. Run duration for these runs was five to six hours. The instability of the cell voltage signal near the end of the run would indicate that metal buildup on the cathodes had reached nearly the maximum before dripping. Power to the cell was shut off and the internal assembly pulled. Most of the liquid aluminum would fall off of the cathodes into the cell container, which would then be lifted from the oven and dumped in a stainless steel pan. Once the bath froze, it would be chipped out of the pan and the produced metal recovered.

The first set of titanium box cathodes lasted 11 runs of an average duration of 5 hours each prior to being replaced due to buildup of a higher melting point aluminum-titanium alloy on the cathode surfaces.

After the first series of runs, similar runs were performed in cell containers of a similar shape but slightly larger and deeper that were fabricated by welding anode alloy plates cast by The Dalles smelter metallurgical department.

After two series of runs with the titanium box cathodes, the cell configuration was changed to two cathode plates of titanium with two center anode plates. In this configuration, the long sides of the run container were util

ized as anodes on one side of each cathode plate with a center anode opposing the other side of the cathode plate. This differed from the prior arrangement in that both sides of the cathode plates were active, while on the center anodes, only one side was active. Upwelling of the bath was on both sides of the cathode plates while downward flow was in the space between the center anodes. The configuration was changed in this fashion due to plans of eventually using TiB_2 cathodes which could not economically be fabricated into the box cathode shape.

Various schemes were tried and abandoned for removing aluminum metal off of the cathodes out of the top of the cell. It was concluded that the only economic way of removing the metal was to find some method of collecting it in the bottom of the cell, so the cathodes were modified to install a drain tip on one end. An alumina boat was inserted in the bottom of the cell prior to insertion of the internal assembly to collect the metal draining off of those tips. Since the bottom of the cast container was sloped downward towards one end, the bottom of the cathodes were sloped likewise to the drain tips at one end and the alumina boat placed such that the drain tips extended down into the boat.

Due to size and spacing, the capacity of the alumina boat was insufficient to allow significantly longer operation. The drain tips on the cathodes served a dual purpose of directing the metal droplets into the alumina boat and maintaining contact with the produced metal so it remained at cathode potential and parasitic currents were avoided.

Although this arrangement proved that metal could successfully be collected in the bottom of the cell without significant alumina sludge accumulation, it did not allow for extended runs. To test for an extended run, the cell container was equipped with a single titanium cathode plate in the center of the cell with a drain tip and an alumina boat. There were no internal anode plates. Although this resulted in a considerable ACD, it allowed room to ladle metal out of the alumina boat with a stainless steel spoon. This run was set up for a longer-term test and fine ore from the smelter dust collector system was fed to maintain 10 to 15% alumina slurry. After approximately 34 hours of continuous operation, the aluminum alloyed with the titanium cathode plate to the point that no further metal would drain to the alumina boat. Shortly after this, the cell experienced a tap out and the run was terminated.

Examination at the end of this run showed heavy alloying on the titanium plate. The tap out was through the side of the container about 2 inches below the bath line and was caused by blister corrosion, a condition where some portion of the anode was not protected by oxide coating and instead would react to form metal fluorides, creating a continuing reaction that expanded in a spherical fashion from the original spot. Several such blisters were found on the inside of the cell container, all at the same elevation below the bath line. One of these penetrated through the side of the cell and resulted in cell termination.

The Goldendale pilot plant procedure of melting the bath components separately from the cell internals along with the utilization of smelter-grade raw materials eliminated the necessity of the bath preparation steps practiced by the Seattle laboratory.

Goldendale Pilot Plant 200 amp cell:

The 200-amp cell was constructed using a high-density alumina cylindrical container purchased from Coors or Vesuvius. The initial containers used were a nominal 7 inches internal diameter and 9 inches tall with approximately a 1/8-inch thick wall. The size of these containers limited the dimensions of the anodes and cathodes such that the capacity of the cell was reduced to 200 amperes at a current density of one ampere per cm^2 on the cathode surface. All active components were suspended in the container from a refractory lid resting on top of the oven cover. For this size cell, the arrangement was two anode plates outside of a single, center cathode plate.

Start up of this cell was similar to the startup used on the metal containers, except due to the more fragile alumina container, the preheat and melting of the NaF and AlF_3 powders was extended to 16 hours. Final melt temperatures were in excess of 800 degrees C to allow the insertion of cold internals and immediate electrolysis.

Initially, the cell ovens were modified by just installing a new top cover with a cutout to fit the diameter of the alumina container and the bottom of the container supported on cast iron plates such that the top inch of the container was within the refractory cover of the oven. This was to avoid cell fumes in the oven that could attack the side radiant heaters. After three test runs that only lasted two or three hours before the alumina container

cracked, it was finally concluded that the portion of the container projecting up into the oven cover refractory was colder than the main portion of the container and that the mechanism of failure was thermal cracking slowly migrating from the top downward.

The setup was then modified by fabricating an 11 inches high copper sleeve to just fit the outer diameter of the alumina containers. This allowed the full height of the container to be within the heated portion of the oven and the copper distributed the heat evenly to all portions of the sides of the container. The copper projected up into the oven cover and was sealed to that cover at the top so cell fumes were still excluded from the oven. This arrangement solved the container cracking problem, although it added a contamination source for copper, since the approximately two inches of copper sleeve projecting above the cell container was unprotected and exposed to the cell fumes.

After resolution of the container-cracking problem, cathodes were fabricated of TiB_2 ceramic to attempt longer runs. The inclusion of TiB_2 in the anode-cathode assembly dictated that these internals be preheated at a controlled rate of approximately 60 degrees C per hour with an argon purge in the second oven to avoid thermal shock that could fracture the cathode.

For these small cells, the cathodes were cut from commercially available $\frac{1}{4}$ -inch thick TiB_2 plates purchased from Ceradyne Corporation. A single 12-inch by 12-inch plate could be cut to supply four cathodes with a nominal 1-inch drain tip, a four-inch high body, and a 7-inch high riser. Anodes of a corresponding shape (without the drain tip) were cut from $\frac{1}{4}$ -inch thick alloy plates cast by The Dalles metallurgical department. The anodes and cathodes were pre-assembled into a rigid assembly with a single cathode bus between to anode buses and appropriate insulators to avoid short circuits and hold the desired ACD. The copper anode and cathode buses were also the support beams for the assembly. The lid of the cell was constructed of high-density alumina refractory board, split to allow placement around the anode and cathode risers, with a removable section for inspection and tapping, and a hole for fume extraction and alumina feed.

Simple bolted connections of the anode alloy risers to the anode bus and the TiB_2 cathode riser to the copper cathode bus were used to complete the assembly. Connections to the anode and cathode bus from the recti

fier were by copper cables, the terminals of which were clamped to the cell buses using vice-grip pliers.

The first run was planned as a 48-hour run and performed as planned for 49 hours before deliberate shutdown. Metal drained off of the cathode into the bottom of the alumina container was maintained at cathode potential by the drain tip on the cathode. The metal was removed with a stainless steel spoon at a fairly frequent rate of every four hours. As the run progressed, high voltage (a nominal $\frac{1}{2}$ volt) developed at the TiB_2 riser to copper bus connection and remained for most of the run. With a current of 200 amperes, this caused this connection to run hotter than desired. Following this run, the connection of cathode riser to bus was modified by electroplating the contact portion of the TiB_2 riser with copper and subsequent runs of this setup had connection voltage drops in the range of 1 to 3 millivolts for the duration of runs in excess of 100 hours.

Initial runs with TiB_2 cathodes did not experience any difficulty with cathodes wetting with molten aluminum immediately upon initiation of electrolysis. Subsequently, when cathodes were manufactured from later procured materials, problems of cathode wetting did occur and necessitated lifting the internals two or three times in the first 24 hours of the run and scraping off any adhering black deposits preventing wetting. Oxidation during upheat in the argon-purged oven was ruled out, since titanium oxide on the surface of the cathode should react with the produced aluminum and not inhibit wetting. Sulfur compounds were ruled out by the temperature to which the bath was heated prior to electrolysis and by analyses of samples taken prior to startup of the cell. It was concluded that the wetting was disrupted due to a condition created in the manufacture of the hot-pressed TiB_2 plates and it was partially resolved by diamond sanding of the cathodes prior to usage.

Subsequent longer runs necessitated that the metal pad be disconnected from the cathode to avoid bath freeze on the accumulated metal. To prevent excessive parasitic currents, the cathode dimension was vertically reduced so that the internal assembly could be raised higher within the limited bath height of the container to provide a longer current path from the bottom of the anodes to the disconnected metal pad and back to the cathode. Tapping on these runs was practiced on 8 to 12-hour intervals. Due to the reduced cathode size, the anodes were correspondingly re

duced and the cell capacity cut back to a nominal 100 amperes at 1 amp/cm².

Later in this series, alumina rings were purchased to extend the top of the container to the top of the copper sleeve. Although this extended height could not contain bath, it allowed the bath level in the container to be raised by approximately $\frac{3}{4}$ inches and reduced the corrosion and flaking of the copper container into the cell bath.

During the development of the 200-amp cells, the necessity of providing a protective sleeve at the bath interface of the anode and cathode risers was determined. This eventually evolved to alumina sleeves from below the bath line through the cell lid on the risers. The anode riser protection was deemed necessary because examinations following prior runs indicated that there was potential corrosion on the anode risers in an area where the anode material was exposed to the bath foam but not protected by oxygen generated at its surface. The protection of the cathode riser was necessary, as the wetting of the cathode by liquid aluminum would migrate to the surface of the bath where it would be re-burned by oxygen in the foam on top of the cell.

The 200-amp cell configuration in a subsequent alumina crucible of 8 inches OD by 11 inches high became the standard "single-crucible" setup for all subsequent tests where a bottom anode was not required.

Goldendale Pilot Plant Double-container cells:

The 100-ampere variation of the 200-amp cell was further modified to test the concept of an active bottom cell that could still be conventionally tapped. This variation involved installing a 5-inch diameter alumina container of 9 inches high within the 7-inch diameter alumina container of the 100-ampere variation. The 5-inch container was spaced approximately 1½ inches off of the bottom of the 7-inch container by a U-shaped carbon chair and offset to one side of the 7-inch container to allow access to the open end of the U-shape between the sides of the two containers. A single hole was drilled in the bottom of the 5-inch container to allow metal dripping from the cathode drain tip to fall through into the 7-inch container in the U-space of the carbon chair.

The first assembly of this concept was with the two containers but without a bottom anode. This was a relatively short run of 49 hours. This setup was subsequently modified by adding a donut-shaped anode plate in the bottom of the 5-inch crucible connected to the anode bus cable by a separate riser of anode alloy sheathed in an alumina tube. With a change to an outer alumina crucible of 8 inches OD by 11 inches high, this arrangement became the standard arrangement for subsequent tests when the test parameters required an active bottom anode. Photographs of this setup are included in a subsequent portion of this report.

200-amp ovens, The Dalles Development Line:

After relocation of the Goldendale pilot plant to the development line at The Dalles smelter of Northwest Aluminum, two new ovens were constructed for a planned series of 200-ampere cell runs. The two ovens of this size from Goldendale were converted into preheat ovens for the internal assemblies to be used in the test runs.

The new ovens were constructed utilizing ceramic-coated half-cylindric heaters to form a heated cylinder heavily insulated on the bottom and sides. The ovens were mounted on the lower platforms of wheeled shop carts. The table top of the metal shop carts was cut to allow the insulated ovens to be jacked up level with the top of the table and refractory insulation board was cut to insulate the table top from the hot zone of the oven. Stainless steel cylinders with a sealed bottom of diameter and depth to allow the alumina run containers to just fit inside of the stainless susceptors were constructed. These were equipped with a top ring that extended out far enough to be supported by the refractory on top of the shop cart table. The result of this arrangement was that the stainless steel susceptor was suspended down into the heated oven from the top ring. The susceptor provided the heat distribution necessary to avoid thermal variations in the alumina container that might lead to container failure and provided a capture mechanism for the bath should the alumina container fail during operation.

The heated oven cylinders were considerably larger in diameter and depth than the cell containers, allowing the potential to use even larger cells by only increasing the size of the stainless steel susceptors.

With more facilities at the development line, the issue of initial cathode wetting was re-addressed and by testing the TiB_2 plate material in liquid aluminum separately from cell electrolysis, a method was developed for chemically cleaning the TiB_2 cathodes prior to use that essentially ended the issue of initial cathode wetting problems.

Rectifiers:

The rectifier used at the Goldendale pilot plant for the 300-ampere and subsequent cells was a Sorenson switching power supply rated 10 volts and 660 amperes. This unit had significant programmable features allowing output to be ramped, cycled, and otherwise programmed, but for almost all of the tests run, the features used were either constant current with voltage limit or constant voltage with current limit. This output of this unit could be controlled from zero amps and zero volts up to its rated capacity and operate into a dead short without damage.

Upon relocation to The Dalles development line, an additional identical rectifier was procured for the 200-amp test cells.

The 5,000-ampere rectifier purchased and used for the 1,000-ampere and 5,000-ampere cell tests was a unit manufactured by Dynapower, air cooled with either 240 or 480 volt three phase input and 24 volt, 5,000 ampere DC output. This rectifier was of the 6-pulse type typically used by the electroplating industry and included controls for constant current with voltage limit or constant voltage with current limit. The input voltage to the transformer was controlled by SCRs to maintain the desired output. This unit was capable of an output range of near zero amperes or zero volts all the way up to its maximum rating and could operate into a dead short without damage. Due to the six-pulse rectification, there were harmonics on the DC output of this unit up to 5% total of the rated current. The primary harmonics were the 5th and 7th, or 300 Hertz and 410 Hertz.

Ore Feeding and Fume Collection:

For all cell configurations, the alumina feed was used as the scrubbing medium to collect fluoride emissions and return fluoride to the cell to avoid this loss affecting bath ratio. For the 200-amp to 300-amp cells, the alumina feed was via a 3/4-inch stainless steel tubing approximately 24 inches long, although at the Goldendale pilot plant, a copper tubing was used.

The discharge of an AccuRate screw feeder was injected into the feed tube at a tee and fell by gravity into the cell via the tube. Off-gas from the cell was extracted by mounting a funnel on top of the tube with a small 12-volt fan with 5 to 7 CFM capacity of the type used for CPU cooling on computers to the sealed top of the funnel. The fan was allowed to pull most of its air from outside of the funnel to keep the fan itself cool. Speed of the fan was controlled by reducing or increasing the voltage to the fan manually based on the desired exhaust temperature from the cell.

On the small cells, no dust collector was used and the volume of the reservoir on top of the funnel was used as a dropout chamber for fines, which were occasionally manually shaken back into the cell. This arrangement was quite effective for returning fluoride to the cell and assisting in maintenance of bath ratio on long test runs. The fans had a tendency to plug because the motors were not sealed and fine alumina particles would get into the simple bearings of the printed circuit motor, so it was not unusual to change out a fan during a run of 100 hours or more. The fans could be cleaned and reused by immersing and running in a container of WD-40.

On the 5,000-ampere cell, a more sophisticated dust collector was used. This cell was equipped with a 10-CFM capacity dust collector consisting of a single dust collector bag rated for particles down to ½ micron. The fixed volume suction fan on this unit was rated for up to 16 inches water column suction and the dust collector was equipped with an air pulse valve that could be operated either manually or automatically based on the pressure drop across the bags. The AccuRate feeder for this cell fed into and tangent to the side of a funnel mounted on top of the feed tube and the dust collector extraction was via a ½ inch diameter tube on an opposite tangent above the feed input. Immediately external to the funnel, a manual valve to allow the operator to bleed outside air into the fume extraction tube was installed and the temperature in the feed funnel was monitored by the datalogger. This temperature was plotted on one of the strip charts on the operator's screen and alarmed for both high and low temperatures. It was desired to maintain the temperature of the fume extraction above 125 degrees C to make sure no moisture from the ore fed plugged the cell feed tube, while at the same time, if the temperature was lower than 80 or 90 degrees C, it was an indication of possible feed tube plugging. The outside bleed air valve allowed the operator to manually adjust the amount of air bled and therefore adjust the amount of fume extraction from the cell

while maintaining the 10-CFM quantity necessary to carry particulate to the dust collector without plugging the fume duct.

Development Line Auxiliary Equipment:

Aside from direct process control and data collection equipment, the development line constructed at The Dalles plant was equipped with two 3-ton capacity overhead bridge cranes, a small programmable milling machine, a lathe, and two metal saws. Other equipment included a TIG welder and a welding chamber that allowed welds to be performed in a controlled atmosphere. A large ceramics kiln was purchased to allow controlled preheating of the internal assembly for the 5,000 ampere cell. An office facility was constructed along with the development line to provide office space, a wet lab, an XRF room (dry lab), a lunch and conference room, and a metering and control room for the computers and rectifier controls. Essentially, the development line had to duplicate all of the functions that are necessary for an aluminum smelter.

Anode casting was performed in one of the metallurgical workspaces associated with The Dalles smelter. The machining, assembly and welding of anodes were performed in the development line shop.

Operational Monitoring:

Bath Ratio and Metal Analyses:

At the Goldendale pilot plant, operation of the inert anode test cells suffered the same handicap as that experienced by the Seattle laboratory, in that data on bath and metal was not obtained for two to three weeks following the completion of a run. Even though the analyses were performed by the Goldendale Smelter's laboratory, the ratios and analyses desired were not covered by their normal equipment and standards, therefore had to be manually determined in the wet lab.

For the development line in The Dalles, an X-ray Fluorescence (XRF) unit was installed to allow elemental analyses of bath and metal within a matter of minutes after the collection of a bath or metal sample. Equipment to crush bath samples, press analyses pellets, and machine metal samples was installed and all operating personnel were trained to use this equipment and perform their own sampling on shift. The data computers were

programmed to allow the operators to input the results of their analyses for data records, automatically calculate bath ratios, and display and print graphs of metal quality or other parameters of interest. The XRF resolved any uncertainty regarding the condition of the bath,

Data Collection:

Data for almost all of the Goldendale test runs and all of the runs at The Dalles development line were collected using Agilent 34970A Data Acquisition Switch Units equipped with one or more 34901A 20-Channel Multiplexer modules. The data loggers were connected to computers via RS-232 serial connections and the recorded voltages, currents, and temperatures were collected using the Agilent-provided BenchLink software.

Although the data loggers had the capability of up to two or three scans per second, a standard scan frequency of scanning and collecting all data points once per minute was established. An independent data logger was used on each cell during its run, so at The Dalles development line, with two 200-amp runs and a 5,000 amp run in progress at the same time, three dataloggers and three computers were required. Due to the large number of thermocouples and temperatures measured on the 5,000-amp cell, that datalogger was equipped with two of its maximum of three 20-channel multiplexers. Detailed measurements were taken on each cell each minute during these runs. Measurements included current, voltage, resistance, temperature, ore feed rate, and comparative current between multiple anodes. Bath samples were generally taken and analyzed each four hours during the run and measured for alumina concentration, sodium fluoride, aluminum fluoride, calcium fluoride and potassium fluoride. Metal was generally tapped at either 8-hour intervals or 12-hour intervals depending on the setup and the test plan. Tapped metal was analyzed at each tap for common contaminants of copper, nickel, iron, silicon, titanium and other potential contaminants if part of the component of the anode or cathode.

Each cell test station was equipped with a data logger, a computer monitor, a keyboard and a mouse to allow observation and analyses of the collected data by the cell operator at the cell. At Goldendale, the data collection computer with a second monitor, keyboard and mouse setup was connected to the cell station by signal splitters and standard cables between the computer in a clean area through the wall to the cell operat

ing area. At The Dalles, the data collection computers were located in a metering room and connected to the data loggers and operator control stations by Avocent Longview Companions, which have the ability to operate a second setup of a monitor, keyboard, mouse, and serial communications connection by a single category 5 Ethernet cable up to a distance of 500 feet from the computer.

The Benchlink software supplied with the dataloggers allowed the creation of a nearly unlimited number of screens to display real-time data. Strip charts were limited to eight channels per screen, but multiple screens were created. Screens were also created to display a digital meter or multiple digital meters, alarms, statistical data, or any combination of meter, strip chart, alarm and statistics. The software allowed simple programming so that signals from the datalogger were manipulated and the results of the calculations displayed real-time on the computer screen. For example, the cell resistance was a calculated value of cell voltage minus the apparent decomposition voltage of alumina divided by the cell current and the value of this calculation displayed was the strip chart and on a meter at the operator's screen. On runs where individual anodes were monitored separately (such as a double-crucible run with two vertical anodes and one bottom anode), the overall cell voltage was a calculated value obtained by multiplying the current and voltage of each anode to obtain the power to that anode, adding these to obtain the total power supplied to the cell, then dividing this by the sum of the currents to obtain the true average voltage of the cell.

For those tests on cells powered by the 5,000-amp rectifier, simple R-C filters were required on the input to the datalogger to compensate for the harmonics from the six-pulse rectifier, since the datalogger scan was so rapid that it would record the peak or valley of the harmonics at the instant of scan. Generally, a 0.3 second time constant was used in the design of the R-C filters to level this harmonic.

At the completion of cell runs, the Benchlink data was exported to Excel spreadsheets for analyses and calculations of current efficiency. The run data for each minute of the run was combined with detail from operators' log sheets and examined for trends and changes. The representative data from each typical 15 minutes of the run as well as the data for any minutes of an occurrence logged in the operators' log sheets were transferred to an Access database. The records and identifications of anode

casting and fabrication data and the cathode data were added to Access database on a relational basis and the results of current efficiency calculations, metal analyses, and bath analyses taken during the run were also attached to this run record. A narrative description of the run was included in the database. Any photos of the run setup taken before or during the run and post-run analyses and photos of anodes and cathodes were also tagged to the Access database records of the run. A printout of the Access database records was combined with printouts from the Benchlink strip charts covering each minute of the entire run and filed along with the operators' run logs in the run data books.

Photos and Graphs:

Figure 8 -This is a photo of one of the anode casings welded by The Dalles metallurgical depart from plates that they cast in heated graphite molds.

Prior to these casings, the initial casings used at the Goldendale pilot plant were of similar size but cast and were of the type shown in the photographs of the Seattle 300-amp cell.

Figure 9 - The photo below is of a titanium cathode box setup from the initial runs at Goldendale pilot plant. The unit is laying on its side in the photo.

Figure 10 -The photo below is a photo of a typical 200-amp cell setup of the single crucible style used both at the Goldendale pilot plant and The Dalles development line. This is a photo of one of the early runs at The Dalles development line used in training additional personnel in assembly

and operation of the 200-amp cell. The photo shows the titanium diboride cathode positioned between two anodes. The centerline of the assembly is offset to one side of the cell to allow room for tapping on the front side in the photo. It is not visible in the photo, but the bottom of the container is sloped towards the near side. This near side pocket has room sufficient for up to 12 hours of metal production and is partially shielded by the nearside anode to reduce parasitic currents. The anode and cathode risers are protected by alumina sleeves from below the bath line up through the refractory lid of the cell. The anodes are perforated to allow flow of bath into the reaction zone and to provide some activity on the back sides of the anode to insure that there is a protective oxygen coating there at all times. This internal assembly was removed and preheated separately before bath powders were added and melted.

The following graph is a plot of the run data collected during the 100-hour run at the Goldendale pilot plant to demonstrate the dynamic range of an inert anode cell to utilize time-of-day electricity. The red line is cell temperature, which was controlled by settings of the cell oven. For most of the run, the temperature ranged between 780° C and 790° C. Current in blue is normalized to current density in amps/cm² and varied from the starting 0.5 amps/cm² for the first 24 hours of operation up to 0.9 amps/cm² in the two days of higher current operation, then back down to the 0.5 amps/cm² for the last day of the four day run.

Figure 11

The black line is the cell voltage recorded each minute during the run. Aside from voltage increases and decreases during current changes, the slight ripple on the voltage chart is due to the resistance change when metal droplets fall from the cathode to the metal reservoir in the bottom of the cell.

The brown line is alumina concentration determined by post-analyses of bath samples taken during the run. This shows that alumina concentration in the bath was generally near 4% by weight throughout the run.

The photo below is of a typical double-crucible setup as used at Golden-dale and The Dalles development line. This setup is limited to approximately 100-amperes at a current density of 1 amp/cm². The outer crucible is the same as the crucible pictured earlier for the 200-amp cell. The carbon chair in the bottom of this crucible supports the smaller inner crucible. Anodes and cathode are smaller to fit the inner crucible, the back anode and the cathode are visible in the photo, along with the anode risers on the right and the cathode riser on the left. One edge of the bottom anode is just visible over the top of the back anode, a later photo shows the bottom anode out of the cell.

Figure 12

The inner crucible and the bottom anode have a hole in the middle that is located directly below the center of the cathode, which has an integral drain tip. The inner crucible is offset to one side of the outer crucible to allow room for a tapping spoon to be inserted to the bottom to extract produced metal. Not shown is a small ($\frac{1}{2}$ " diameter) hole in the upper back side of the small crucible that is a bath equalizer so that metal can drop through the bottom of the inner crucible without any pressure restrictions.

Figure 13 - This is the bottom anode from the setup on the prior page.

Figure 14

Figure 14 on the prior page is the plot of Run 55 at the Goldendale pilot plant. This was the first extended run of the double crucible setup with a bottom anode. Again, the red line represents cell temperature and ran around 780° C for the duration of the 4 day run. The blue line is current density, which was started at 0.5 amps/cm² on the vertical anodes and then moved up in stages to 0.75 amps/cm² on the vertical anodes. The green line is cell voltage and the black line is cell resistance on an expanded scale. Early in this run, the cathode was not completely wetted and in the first day of operation, it was pulled and deposits scraped from it three times.

The ripple on voltage (magnified on the resistance scale) represents metal droplets falling from the cathode and into the outer reservoir. As metal builds up on the cathode, the cell resistance slowly lowered due to reduced ACD. When a droplet falls, the resistance jumps due to the sudden change in ACD.

On a stable cell, the metal droplets are all nearly the same size, so current efficiency can be estimated by the time period between drops.

As can be seen from the graph, the last two days operation of the cell were very steady and at good current efficiency. The other noteworthy item is that for the last two days, the resistance was steady or slightly declining, indicating that the anodes had stabilized.

The brown line represents alumina concentration determined by post-analyses. As may be expected, with the agitation of a bottom anode, the alumina in suspension exceeded the solubility of the ore at the cell temperature.

The next sequence of photos represents the progression of metal quality efforts utilizing the 200-ampere cell shortly after development was relocated to The Dalles development line. Graphs are self-explanatory. Tapping was performed on 8-hour or 12-hour intervals and the metal elements of the anodes and cathode were measured and recorded. Elements of the tapping ladle (molybdenum) and silicon from the smelter AlF₃ used to create new bath at the start of the run are not shown, since moly is not a normal contaminant and silicon is a known value based on aluminum fluoride usage in normal smelting.

Figure 15 (above) & Figure 16 (below)

Figure 17

In the previous graphs, each metal element of the anodes and cathodes (copper, nickel, iron, and titanium) are shown individually in percentage by weight of metal tapped and the black graph represents the sum of all of these, or the total contamination by elements of the anodes and cathode. The value for iron also includes any iron in the smelter-grade alumina used to feed the cells during the run. The solid line at the 0.25% level represents commercial grade aluminum (99.7% pure) with an allowance of 0.05% for typical silicon contamination, or a purity of 99.75% to be met or bettered for contamination from anodes and cathode.

Some tests were performed with modified baths where 50% to 75% of the NaF was replaced by KF. On the following page is a graph of one of these runs. As typical with potassium-containing bath, the run shows improved metal quality and lower current efficiency than NaF-AlF₃ bath.

Only limited testing was performed with potassium baths, since it was judged to not presently be economically feasible for a number of reasons.

Figure 18

In this run, even the starting tap quality was better than commercial grade aluminum and approached 99.95% purity as far as anode and cathode elements towards the end of the run. Iron contamination due to iron contained in the alumina was estimated to be 0.02% on the average and this should be taken into account when examining the previous quality charts with respect to anode corrosion estimates.

After completion of metal quality evaluations, efforts concentrated on casting anode plates and the fabrication of anode assemblies for the 5,000-ampere cell. The following photograph shows a completed 5,000-ampere anode assembly. As with the anodes in the smaller cells, the active anodes in this assembly were perforated with a multitude of small holes to improve bath circulation and provide some activity for the back sides of the anodes. The assembly pictured was finalized with the addition of three cathode plates. The 5,000 amp assembly was considered to be ½ a module of a future 100,000 to 150,000 amp cell, in that a full module would consist of six cathode plates and 12 anodes in an anode box and that module would be replaceable in a cell containing 10 to 15 modules.

Figure 19 - 5,000-amp anode assembly

In this photo, the eight anode risers are shown with the alumina sleeve guards at the bottoms of the risers, but the alumina sleeves have not yet been installed. The anode box is formed of the same alloy as the anodes and the entire assembly was submerged in the bath to a depth approximately six inches above the tops of the anodes. There are two anodes for each cathode and there is an intermediate brace between adjacent anodes. The side plates of the box are not active. The end plates of the box (where the risers attach) are active to the edges of the cathode. Each cathode was equipped with three drain tips for a total of nine drains and the bottom plate of the box (also active as an anode) was drilled with holes corresponding to the metal drains from the cathode.

Anode plates were cast to a dimension of 24 inches by 24 inches. Each cast plate allowed the manufacture of two anodes, or two side & end plates, or one bottom plate. The anode risers were cast as rectangular bars 28 inches long and then machined to final dimension. The tapping side of the anode box was offset from the refractory walls of the cell to

provide room for metal removal and some holes were added to this side to guarantee circulation of alumina-containing bath.

The following photograph is of one of the Development line 200-amp cells

Off-gas cleaning

- Sealed cell, crustless with continuous feed
- Alumina scrubbing on each individual cell
- Collects up to 99.9% F from off-gas
- Stabilizes bath ratio by returning F from each cell to that particular cell
- A 100kA cell off-gases a theoretical maximum of 13 SCFM.
- Modern prebake collection systems @ 3,000 SCFM per cell.

Figure 20

in operation, showing the ore feeder and scrubber system. The features of this scrubber system are detailed in the side bar adjacent to the photograph.

On the following page is the chart from one of the development line runs where the dynamic range of an inert anode cell is demonstrated. This is the same run that was the first concerted attempt to prove good metal quality. At the end of the planned 72 hours of operation, the current was increased from the standard 0.75 amps/cm² test to 1.0 amps/cm² for the remainder of this 100-hour run.

The response of the cell to this change is shown on the run chart produced from the datalogger results.

Figure 21 - Cell response to dynamic load change

As can be seen in the above run chart, when the current was increased at from 0.75 amps/cm² to 1.0 amps/cm², the cell resistance momentarily increased, then returned to a range actually below where it was at the time of the increase. The temperature was held in the planned range by the automatic controls on the cell oven. Metal quality did not appear to suffer, although the amount of anode metals increased, due to the increased production of aluminum, the relative concentration of impurities did not significantly change.

On the following page is an expanded detail of the area of the step change in current.

Detail at dynamic change

Figure 22

This chart shows the eight hour period incorporating the current step change. The sawtooth on the cell resistance is the effect previously described of metal droplets falling from the cathode and creating a step change in ACD. As can be seen after the current increase, the frequency of these drops also increased and comparison of the period of these drops indicated that the current efficiency did not significantly change when the current was increased.

Section 3 - Comparison of Inert Anode Development progress to February 1998 Inert Anode Roadmap:

The Inert Anode Roadmap document was created through joint collaboration among representatives of the nine primary aluminum producers, the Department of Energy, and the Aluminum Association. In brief, it identifies the potential benefits of inert anode technology, the difficulties to be overcome, and a sequence of development steps considered necessary with criteria to be met to achieve success. The Roadmap is predisposed towards existing Hall-Heroult technology with respect to bath composition, operating temperatures, controls, and arrangements, although it does allow options for different bath composition, temperatures, and wetted stable cathodes.

Following are excerpts of important technical criteria from the Roadmap and a subsequent comparison with results achieved in the NAT inert anode development program:

Excerpts:

(1) Inert Anode technology, coupled with that of stable, wetted cathodes, offers the greatest opportunity to improve cell efficiency and lower primary aluminum production costs.

(2) On carbon anodes the oxygen of alumina is discharged but reacts with the carbon and forms carbon dioxide, which decreases the decomposition potential by about a volt. Such depolarization does not occur in inert anodes. Oxygen is evolved at the standard decomposition voltage.

(3) [Inert Anode Technology] benefits are expected to fall into the following categories:

- *Cost/Productivity*
- *Process Simplification/Control*
- *Energy Reduction*
- *Elimination of Greenhouse Gases*
- *Other Environmental Benefits*

(4) While no single new technology must meet all of these requirements in order to be considered successful, the degree of success may be measured by how many of the requirements are indeed fulfilled.

(5) To measure the benefits of the new anode technology (used in conjunction with wettable cathode technology), a comparison will have to be made not just against current technology but also against a cell operating with conventional anode technology and potential wettable cathode technology.

(6) The dimensionally stable flat bottom of the new anode would enable better control of the anode-cathode distance. In general, the technology should provide more precise anode-cathode distance control, although it would not eliminate problems with magnetics in regard to the molten metal.

(7) The potential for energy savings definitely exists for the combination of non-consumable anodes and dimensionally stable cathode technology. Some of this depends on the activity of the oxygen present in the cryolite bath versus the reactivity of carbon dioxide, which is not completely understood at this time.

(8) A possible additional benefit of combining non-consumable anode technology with wettable cathode technology would be a reduction in the amount of spent potliner that is generated, although this is somewhat speculative.

(9) A number of performance criteria or targets have been defined for inert anode technology and then screened to determine their level of importance to the technology's success. Two sets of performance targets have been defined:

- Essential (first-tier) targets*
- Beneficial (second-tier) targets*

(10) The "essential" or first-tier targets are primarily technical criteria that absolutely must be met by the technology.

(11) The criteria discussed in this section actually apply to an inert anode system.

(12) The essential characteristics for anodes are electrochemical and thermodynamic stability, electrochemical behavior, electrical conductivity, mechanical properties, oxidation, metal quality, and environmental and safety acceptable material.

(13)

Essential (1st Tier)	
Criterion	Target for Inert Anode
<i>Electrochemical and thermodynamic Stability</i>	<i>Erosion rate of <10mm/yr with current density (0.8 amps/cm²)</i>
<i>Electrochemical Behavior (Current Density)</i>	<i>Polarization voltage of <0.5 volts at 0.8 amps/cm²</i>
<i>Electrical Conductivity</i>	<i>Voltage (continuous) drop no worse than with carbon anodes -bus to electrolyte</i>
<i>Mechanical Properties</i>	<i>Sufficiently robust to survive in normal plant conditions -must withstand cell vibrations -must support own weight -must maintain mechanical integrity -must not suffer from thermal shock -must survive in normal bath -must handle heat up from room to operating temperature range of 930°C-1100°C</i>
<i>Oxidation</i>	<i>Stability in oxygen at 1,000°C -should not spall may be a higher/lower operating temperature</i>
<i>Metal Quality</i>	<i>No worse than today's quality -0.1% Fe, 0.2% Si</i>
<i>Environmental and Safety Acceptability of the Material</i>	<i>Eliminate beryllium, chromium, radioactive and EPA-defined hazardous materials.</i>

(14) Past research efforts have tended to overlook two critical points:

- *Aluminum and sodium are soluble in the cryolite bath, which can lead to the formation of a concentration and diffusion gradient in the cell that can interact with the electrode*
- *Aluminum and sodium confer electronic conductivity upon the electrolyte*

(15) *The rate of oxidation of carbon to CO₂ in the cryolite bath is so great that there is never an electronically conducting interface in current carbon anodes. Given this situation, tests of new systems should include saturation of the test cell with aluminum or sodium to show that there are no excursions in voltage.*

(16) *“Erosion rate” has been chosen as the criterion for measuring stability; metal quality (discussed later) is also a key indicator of anode performance. The specific target is **an erosion rate of less than 10 mm/year**, which contains some slack for adjustments to the bath. Any inert anode material developed during earlier investigations should meet this criteria or be ruled out for further consideration.*

(17) *The current density capability/capacity of the inert anode is a major component of electrochemical behavior, conventional anodes tend to operate at approximately 0.8 amps/cm². Specifically, the polarization voltage, which must be added to the 2.2 volts alumina decomposition voltage, must be kept to a minimum. The performance criterion defined is a **polarization voltage less than 0.5 volts at 0.8 amps/cm²**.*

(18) *The new system must pass the electrical current from the connecting busbar to the actual double layer in the electrolyte on a continuous basis at a reasonable cost, while avoiding a conductivity problem at the interface between the busbar and the top end of the anode. In present cells, the voltage drops in the anode are on the order of 0.25 to 0.45 volts. Because the nature and thickness of the new material are unknown, the anode should have a voltage drop no greater than in the present cell, or else there is no gain in efficiency.*

(19) *The new material also must be continuously conductive over the life of the anode. The material must behave like carbon in a reproducible way, with a **total voltage drop that is no worse than can be achieved with carbon at the current densities used today with carbon anodes**.*

(20) *Since any new material in a retrofit application will have to pass through ambient air and the crust, to make contact with fluoride vapors, oxygen, liquid fluoride, heat and crust, the material must be resistant to oxidation to ensure the quality of the molten metal. The actual performance criterion is that **the material should not spall in oxygen at 1,000° C**. While it is acknowledged that operating temperature conditions for baths may actually be lower than 1,000° C, an anode is likely to be exposed to temperatures approaching 1,000° C sometime during its life.*

(21) *The criterion for metal quality is that it must be no worse than the quality of present-day metals. The metal can become contaminated with almost any element at concentrations of up to 0.1 percent before the quality of the hot metal is affected; specified limits include concentrations of 0.1% iron and 0.2% silicon.*

(22) *Some of the most critical barriers to the success of inert anode technology exist because a “viable” material for fabricating the anodes has not yet been demonstrated. Other materials barriers include the inability to achieve adequately high erosion or wear characteristics at the frozen crust-electrolyte interface, and the need for defining a screening test for these characteristics.*

(23) *There is also little information on the activity of oxygen versus carbon dioxide under operating cell conditions, which prevents a complete understanding of the details of the electrolysis process using inert anodes. It is unknown, for example, whether oxygen will be so reactive that it might reduce current efficiency.*

(24) *Present aluminum feeding-control systems are another technical barrier because they do not eliminate anode effects. Inert anode technology itself is not enough to eliminate these disruptions. The electrical connection to the anode is yet another technology gap.*

(25) *In addition to other problems with anode materials discussed earlier, other material problems exist within the system, particularly for freezeless operation of the cell. If net energy efficiency is an essential goal, freezeless operation will be necessary.*

(26) *Another anticipated requirement for high system efficiency is multi-polar operation. Several technical barriers are associated with multi-polar operation, particularly gas flows and current efficiency.*

(27) *The industry feels that there has not been enough consideration of design parameters apart from the anode that might make the anode itself more viable. An extreme example would be to produce aluminum at temperatures below its melting point; another possibility could be to keep the cell hot but cool the anode.*

(28) *Research efforts selected for funding then would proceed to the bench-top testing stage. The major requirement here is that the anode must be tested at 100 amps for 100 hours.*

(29) Is there a critical point at which researchers should consider merging inert anode technology with wettable cathode technology? Experience has shown that when technologies are combined, the chances of success go down dramatically, although the combination of these technologies could become the potential goal if the results of bench-top testing are favorable.

(30) The laboratory pilot test of the inert anode must take place at 1,000 amps for 1,000 hours.

(31) The requirements for the pilot test are to operate 10,000 amperes for 10,000 hours.

Comparisons to results achieved:

Inert anode development work performed by Northwest Aluminum Technologies primarily concentrated on combining inert anode technology with wetted cathode technology and at lower operating temperatures than originally envisioned by the Roadmap. This work was within the scope of the Roadmap, however, as detailed in excerpts (1), (4), (5), (7), (8), (27), and (29).

Almost all NAT anode development work was with anodes fabricated from metal alloy mixtures, primarily alloys of copper, nickel and iron. The NAT Seattle laboratory tested both cast and sintered anodes of these alloys while the development work at the Goldendale pilot plant and The Dalles development line was almost exclusively with cast alloys prepared in-house. Some tests at The Dalles were performed with an alloy that was cast and hot-rolled by an outside vendor. Although tests outside of these ranges were performed, the general range of alloys tested in the pilot plant and the development line was 20% to 65% copper, 15% to 60% iron, and 20% to 50% nickel. Within these ranges of anode materials, the Essential Criterion of Electrochemical Behavior (Polarization voltage of <0.5 volts at 0.8 amps/cm^2) was never exceeded. Typical zero-intercept voltages at current densities in the range of 0.75 to 0.85 amps/cm^2 were measured at 2.46 volts, which includes the 2.2 volts required for alumina decomposition. The polarization voltage for all anodes in these alloy groups ranged from 0.18 volts at 0.25 amps/cm^2 to 0.28 volts at 1.0 amps/cm^2 . These results compared favorably with the criteria expressed in excerpts (5), (9), (10), (11), (12), (13), and (17) and are well below the criterion of 0.5 volts which must be met. The casting of anode plates in excess of four square feet per side was performed in-house with induction melting and casting in graphite molds. This resolves the fabrication concern expressed in excerpt (22).

Several excerpts from the Roadmap refer to uncertainties regarding the reactions of oxygen in the bath with metal product and of an electronically conducting interface, which may exist in the absence of carbon in the cell. Should oxygen react with the metal product or should there be an electronically conducting interface in the bath, then current efficiency of the inert anode cell would suffer correspondingly. In a large number of test runs at The Dalles development line, these concerns were shown to be groundless. Current efficiencies in excess of 92% were routinely demonstrated. For example, in June 2003 Run A41 was operated at 150 amperes for total period of 270 hours (11 days). Overall current efficiency for the entire run was in excess of 94%. Average current efficiency for all taps for the last 250 hours of the run was in excess of 95%. These results compare with the concerns and criteria expressed in excerpts (15) and (23).

One of the Essential Criteria to be met by inert anode technology is identified as "Erosion rate of <10 mm/yr with current density of (0.8 amps/cm^2) ". In part, the specific of 0.8 amps/cm^2 in this criterion is based solely upon conventional carbon anode technology since this is the typical operating level of conventional smelters. There is nothing inherent in inert anode technology that dictates a specific current density. At the Goldendale pilot plant and The Dalles development line, inert anode test cells were operated at current densities ranging from 0.23 amps/cm^2 through 1.05 amps/cm^2 . The term "erosion rate" implies a wearing away of the anode material by mechanical abrasion, whereas in NAT's development work, it is believed that "corrosion rate" would be a more appropriate measure. In either case, the physical measurement of this parameter cannot be directly performed. In the typical operation of a metal alloy inert anode, the surface of the anode is oxidized into a conductive metal oxide layer that subsequently protects the underlying metal. Oxygen diffusion through this layer into the base metal increases the layer thickness while corrosion or dissolution into the bath of the oxide layer decreases the layer thickness. Physical measurements of anodes following extended runs may indicate an increase in thickness of the anode plates and/or an increase in weight. If the oxide layer is cleaned to bare metal, then a loss of weight or a decrease in thickness can be measured, but this loss cannot be necessarily attributed to cell operations. Numerous extended runs (100 hours or greater duration) were performed at The Dalles development line at currents in the range of 100 to 200 amperes and current densities of 0.5 amps/cm^2 to 1.0 amps/cm^2 where overall metal quality with respect to the anode alloys of copper, nickel and iron show less than 0.1% aggregate contamination by all of the elements in the anodes and cathodes. These results were achieved with smelter-grade sandy alumina, smelter-grade aluminum fluoride

and smelter-grade sodium fluoride bath materials, all of which have some levels of iron, silicon, titanium, and other metallic elements. These runs were performed with dry scrubbing on the cell and all metal produced drained to the bottom of the cell and completely removed with each tap. Any anode alloy losses in this circumstance must end up in the metal produced. Based on numerous high-purity runs, the combined anode corrosion, spalling, and erosion rate was approximately 2.4 mm/year at 0.5 amps/cm² and 4.8 mm/year at 1.0 amps/cm², well within the criterion of <10 mm/year at 0.8 amps/cm². These runs also fulfilled the criterion of metal quality equal or better than today's conventional metal quality. Runs A06 and A14 at The Dalles development line are examples of runs with low erosion rates and high metal purity in a "cryolite" bath. These results resolve the concerns expressed in excerpts (10), (12), (13), (16), (20), and (21).

The Roadmap implies that inert anode results must be in a "normal" or "cryolite" bath to be considered successful. Since almost all conventional commercial operations run with an excess of aluminum fluoride and with some level of calcium fluoride in the bath, the "cryolite" bath requirement should be interpreted to include baths based on a mixture of sodium fluoride and aluminum fluoride with calcium fluoride and perhaps potassium fluoride at levels consistent with their occurrence in conventional alumina feed. The lower operating temperature operation used by Northwest Aluminum Technology was a cryolite-based bath consisting of sodium fluoride and aluminum fluoride with an excess of aluminum fluoride compared to pure cryolite. Test runs were performed with calcium fluoride added to represent the estimated steady-state operating concentration due to the presence of calcium in the alumina. The majority of all runs practiced at the Goldendale pilot plant and The Dalles development line were with cryolite-based bath of these compositions and therefore were in agreement with excerpts ((7), (13), (14), and (15).

Electrical conductivity of the bus to electrolyte should be no worse than with carbon anodes and the mechanical properties of the anode should be sufficiently robust to survive in normal plant conditions. The metal alloy anode compositions used by Northwest Aluminum Technologies at the Goldendale pilot plant and The Dalles development line were all considerably more conductive than carbon anodes and had superior mechanical properties. Connection of the anodes to the anode bus was by simple bolted connections of the anode material itself to the bus. Voltage drops from bus to electrolyte depended on the selected cross-sectional area of that portion of the anode material used as an electrical riser, but typically were in the range of 0.1 volt to 0.25 volts, considerably less than that of conventional carbon anode assemblies. Generally, the selection of the cross-

sectional area was based more on thermal conductivity and heat loss considerations than on electrical drops. These results address the concerns expressed in excerpts (12), (13), (18), and (19).

The Roadmap devotes considerable attention to the issue of retrofitting an existing carbon-lined cathode with a new inert anode and specifies that the inert anode technology should provide more precise control of anode-cathode distance. Retrofitting with a horizontal cathode configuration does not resolve the problems of molten metal reaction in the heavy magnetic fields nor allow achievement of minimum anode-cathode distances and lowest possible bath resistance drops. In addition, the continued use of a carbon cathode would not avoid the generation of the large amount of hazardous waste currently associated with the rebuilding of smelter cathodes. The bi-planar horizontal arrangement does not permit maximum effective usage of physical space and retrofit applications would continue to require a heavy insulating crust and bath freeze around the sides of the cathode to protect the carbon liner. These concerns are expressed in excerpts (6), (20), (22), (24), and (26). Excerpts (1), (7), (8), (25), (26), (27), and (29), however, indicate that the eventual economic success of inert anode technology will likely be in conjunction with stable, wettable cathode technology.

All Inert Anode testing at the Goldendale pilot plant and The Dalles development line was in conjunction with a fixed wettable cathode in a vertical multi-planar arrangement. This arrangement provides for a fixed and minimum anode-cathode distance that was unchanged through the duration of cell operations. Combined with a low bath ratio and low temperature operation, this arrangement allowed for a tightly sealed cell that operated in a crustless mode. The metal produced was drained from the active portion of the cell and was not at cathode potential. This, combined with operations at temperatures many degrees above the freezing point of the bath allowed for controlled continuous alumina feed, the elimination of anode effects, high current efficiency, and efficient utilization of physical space. The high rate of bath circulation in the cell ensured that alumina was rapidly and consistently distributed and that localized bath ratio gradients were minimized or eliminated. Operation in crustless mode provided the potential for a much greater dynamic current range for the cell with the possible economics of utilization of available interruptible electrical supply sources. Cell temperature control was by external cooling rate control. Test runs were performed during which inert anode cells were successfully operated up and down over a current range of 0.5 amps/cm² to 1.0 amps/cm² to approximate weekday high-cost power and weekend low-cost power availability. Many test runs were performed of 100 hours or greater duration at currents ranging from 75 to 200 amperes. All of the

requirements for success of the bench-top testing stage, as detailed in Roadmap excerpt (28), and the Essential first-tier targets as detailed in Roadmap excerpt (13), were met.

The inert anode cell with metal alloy anodes and fixed ceramic cathodes does not generate spent potliner and therefore avoids this major industrial source of hazardous waste. Since the cell does not generate CO₂ or fluorocarbons, it does not contribute to the generation of global warming gases.

Section 4 - Conclusions:

Significant successes achieved:

The inert anode research and development activities achieved the following significant successes:

- Basic research identified many of the mechanisms for the reactions at the anodes and cathodes of the inert anode cell and verified that reasonable current efficiency and metal quality could be achieved.
- Research into the alloys of copper, nickel and iron identified those compositions with the most promise to act as long term, stable anodes in aluminum reduction.
- Methods were developed to seal, collect emissions and scrub the emissions from the low temperature inert anode cell. The method developed also provides for the automatic continuous feeding of the cell and allowed the return of fluoride emissions directly to the cell permitting more precise control of bath chemistry.
- Methods were developed to collect and tap metal by conventional means from a cell with an active anodic bottom.
- Control systems were developed and proven to allow rapid and accurate measurement of bath chemistry, including alumina concentration, calcium level, bath ratio, and bath contaminants. These systems are sufficiently responsive to maintain the tight control necessary for the narrow operating range of a low temperature cell.
- High quality metal was produced using metal anodes, economical smelter-grade alumina, commercial-grade bath materials, and dry scrubbing.
- Current efficiencies equal or better than that of conventional smelter technology was demonstrated in long runs of the development cells.
- Methods were developed for the successful casting, machining and welding of the metal alloys suitable for inert anodes.

- The potential for low energy consumption was demonstrated along with a newly identified potential for significant utilization of low-cost interruptible power on a time-of-day basis or instant availability basis.
- All Essential First-Tier targets of the Inert Anode Roadmap were met.
- A method of performing a stable high-quality, low resistance electrical joint to TiB_2 within the high temperature environment of the cell was invented and demonstrated.
- A number of additional developments necessary for the commercialization of inert anode technology and low temperature electrolysis of aluminum were identified.
- The mechanisms of bath freeze on a cathodic metal pad were identified and verified by research analyses of the frozen cell method. The solution to this problem was found to be disconnection of the metal pad from the cathode potential and methods were developed to greatly reduce and eliminate parasitic current losses with a disconnected metal pad.
- The solubility of aluminum in low temperature baths was found to be low, which provides a potential for high current efficiencies. This was verified in development testing where even small, bench scale cells were operated at current efficiencies up to and in excess of 95%.

Potential Energy and Energy Cost Savings with Low Temperature Inert Anode Technology:

Three major areas of potential energy benefits were identified in the course of NAT's low temperature inert anode electrolysis investigation. The first area is in direct savings of the energy required for the reduction of alumina to primary aluminum. In development operations, with small ACD's ($\frac{1}{2}$ ") and low current densities (0.23 amps/cm^2), aluminum metal could be produced at voltages as low as 2.93 volts. This low voltage was achieved in an externally heated cell, however, and could not be realized in a commercially viable operation. The calculated break even energy requirement to overcome the alumina decomposition voltage and other energy requirements to bring the alumina up to temperature and dissolve it in the bath indicate that the minimum voltage requirement is 3.07 volts. To this must be added any anode or cathode over-voltages, bath resistance drops, and energy lost during the removal of cell off-gases and liquid aluminum.

Although theoretically possible to provide heat to the cell by fuel-fired techniques and thereby improve overall energy efficiency by eliminating losses associated with the generation of electricity, from a practical standpoint, the heat required to maintain operating temperature in the cell should also come from the supplied

electricity. It is therefore difficult to visualize a cell which would operate on less than 3.4 volts, no matter how heavily insulated, since the electrical conductors to the anodes and cathodes required to achieve extremely low cell voltages are also very good heat conductors and if these are designed for low voltage drops, they are large heat sinks.

If a cell voltage in the range of 3.4 to 3.6 volts is achievable, this represents approximately a 10% to 15% improvement over present best smelter technology, which is estimated to require a cell voltage of 4.0 volts. Present technology obtains a benefit of the negative decomposition voltage of the carbon-to-carbon dioxide reaction due to consumption of the carbon anodes. This reaction also generates heat beyond the value of the composition voltage that it adds back to the cell, so the burning of the carbon contributes to the heating of the cell and overcomes much of the heat loss due to heat conduction by the electrical conductors.

There are other potential energy savings that have been identified with the inert anode technology, however, and these may be of bigger benefit than the direct energy savings. The second energy benefit is the potential for utilization of time-of-day electricity. Particularly in large, thermal power systems, off-peak electricity can be purchased at a considerably reduced rate from the cost during peak hours of usage. It takes capital investment, operators, maintenance, and fuel to produce electricity in a large steam power plant and the generating capacity must be available to meet the highest expected demand on the system. This requires capital investment, operators, and maintenance. Since many hours are required to bring a steam plant up to full capacity, it cannot be shut down just because demand drops for a few minutes, a few hours, or even a few days, so the operators and maintenance wear and tear continue even when loads drop. Fuel efficiency also drops as load drops, since parasitic loads such as cooling towers, feed water pumps, environmental controls, and even the power plant's own lighting are required whether the total load is high or low. The only direct savings of reduced load are in fuel consumption and some savings in environmental chemicals.

During NAT's inert anode development, the ability to vary the consumption of electricity in the cell upon short notice as much as 100% (from 0.5 amps/cm² to 1.0 amps/cm²) was demonstrated on several occasions. This provides the potential of constructing an inert anode style smelter that could utilize a minimum amount of power during daytime weekday peaks and double its production during off-peak hours at night and on weekends. With today's available computerization and interconnected distribution systems, it would even be possible for such a

smelter to pick up the excess created by the temporary shutdown of a large motor hundreds of miles away and utilize that energy for the 30 minutes that the unit was off-line.

Figure 23

Comparison of an existing smelter to an equivalent Inert Anode smelter

This chart shows the approximate advantage of both decreased electrical usage of an inert anode plant and decreased electrical cost in comparison to an existing US smelter of the same capacity running steady at 100% capacity. The inert anode plant would operate at 60% of the normalized capacity for 8 hours per day and at 120% for 16 hours per day. Compared to the existing smelter requiring 4.7 volts per cell, the inert anode plant requires 3.5 volts during low current operation but higher voltage in the range of 3.9 to 4.0 volts during high current operation. The high current operation corresponds to the low electricity cost period. The combined energy savings and cost savings represents nearly 57% cost reduction for electricity over the existing US smelter. In actual operation, the inert anode plant would also run at the 120% capacity level on weekends and holidays for additional savings.

Potential Locational Advantage of an Inert Anode smelter:

The present best smelter technology is considered to be large cells utilizing complex bus design to compensate for magnetic field effects and pre-baked carbon anodes. The anodes for the most modern prebakes are fabricated from coal tar pitch and calcined petroleum coke, formed in extremely large hydraulic presses or large, special-purpose vibrating compactors to precise dimensions, then baked in gas-fired refractory furnaces to temperatures in excess of 1200° C. The overall cycle for the fabrication and baking of one anode is approximately 21 to 30 days. The anode is not completely consumed in the reduction cell and generally an anode residual of 15% to 25% by weight of the original anode is removed. This material is re-crushed and reused in the manufacture of subsequent anodes.

The anode plant for a modern prebake smelter is large and complex. Net anode consumption is approximately 0.42 to 0.44 kg of carbon per kg of aluminum produced. The anode plant in combination with the anode rodding room for inserting the electrical connectors into the anodes represents up to 40% of the capital cost of a new smelter. Considerable raw material handling facilities are necessary in terms of storage silos, heated tanks to store coal tar pitch, rail or ship transport and unloading facilities, conveying systems, and scrubbing systems for the anode fabrication and baking facilities to collect and dispose of carcinogenic coal tar pitch volatiles. In addition to the capital and environmental costs, energy is required to operate the machinery of the anode plant, to maintain the liquid pitch at temperature, and to fire the furnaces to bake the anodes. This energy must be added to the electrical energy required for smelting to evaluate the overall energy consumption of the modern smelter. A value of 0.44 to 0.66 kilowatt hours per kilogram of aluminum produced is generally used in this evaluation. This alternate energy consumption is equivalent to approximately 0.17 additional cell volts in comparison to an inert anode plant.

The modern smelter also requires large and complex fume scrubbing systems for the reduction cells. A typical modern prebake plant will have a complex series of large ducts collecting in the range of 4,000 to 6,000 NM³/minute of off-gas from the cell that must be scrubbed to clean gaseous and particulate fluorides. The energy consumption of these facilities must be added to the energy required for the cells and the mill power requirements of a large smelter can represent at least 5% and sometimes as much as 10% of the process power requirements to operate the cells.

The anode plant primarily and the scrubbing systems secondarily determine the economic size of a new smelter, which is presently estimated to be an annual capacity of 250,000 or more metric tons per year. A plant of this size requires a steady, reliable electrical supply of approximately 410 megawatts. These plants are physically quite large with considerable land areas required for electrical switchyards, incoming high voltage transmission lines, rail yards for raw materials, smelter buildings of up to one kilometer in lengths, and the necessary storage silos and casting facilities. In spite of the sophisticated and expensive emissions scrubbers, the plants still emit low levels of fluorocarbons, fluorides, coal-tar pitch volatiles and particulates that restrict their locations to relatively remote or rural areas. The spent potliner from conventional aluminum smelters is a listed hazardous waste and must be handled and disposed accordingly, which also involves locational restrictions, hazardous waste manifesting and transportation, spill prevention and control, and, of course, considerable added expense. The economic-size smelter generates approximately 8,600 tons per year of spent potliner.

In comparison to a conventional prebake smelter, an inert anode facility would not require an on-site anode facility and one or two railcars per year of anodes would satisfy the requirements of a reasonably large inert anode smelter. In addition, the scrubbing system required would be much smaller and less complex. A 100,000-ampere inert anode cell would produce approximately 13 standard cubic feet per minute of oxygen that must be removed from the cell. Assuming double that amount of extraction to account for duct leakage and other sources, this amount represents approximately 1% of the off-gas collection requirements from a prebake cell of the same size. The dry scrubber system of the totally sealed inert anode cell is incorporated in the cell feed system and this collects and recycles over 99% of the fluoride and bath vapor emissions from the cell. The remaining emissions, consisting primarily of fine alumina particulates carried over from the feed stream, would be ducted to a central dust collecting plant where final scrubbing, if necessary, would be accomplished. This plant would be very small compared to the aggregate scrubbers of a prebake smelter. The inert anode cell generates no spent potliner, no coal tar pitch volatiles, and no fluorocarbons.

The elimination of the anode plant and the large, complex scrubbers changes the economics of the aluminum smelter. The two major items that dictate the economic size are removed from consideration. The elimination of objectionable environmental items and the significant reduction in the overall sizes of comparable facilities also eliminate many of the locational restrictions. It therefore would be

come feasible to consider the construction of smaller aluminum smelters adjacent to the users of primary aluminum, even when those may be in the center of urban areas. A smaller aluminum smelter, particularly one whose electrical load could be varied at will over a wide range, would be able to take advantage of power systems that had excess power available in smaller quantities than the output of an entire major power plant. In combination with simple, gas-fired peaking power backup facilities, such a plant could function to utilize the spinning reserves presently required of commercial power systems at greatly reduced electrical costs and transmission requirements.

Environmental benefits:

The basis of the environmental benefits was previously detailed. Benefits include:

- Elimination of spent potliner, a major source of hazardous waste.
- Elimination of fluorocarbon generation, a contributor to ozone depletion.
- Elimination of carbon dioxide emission from the reduction cells, a reduction in the generation of green house gases.
- Reduction in particulate emissions due to completely sealed cells, enclosed alumina handling facilities, and a great reduction in the amount of off-gases cleaned and discharged.
- Reduction in transportation requirements for coal tar pitch, calcined petroleum coke, and spent potliner disposal.
- Reduction or elimination in the usage of chemicals such as sodium hydroxide used to scrub emissions from aluminum smelters.
- Elimination of CTPV (coal tar pitch volatiles) presently emitted from anode baking facilities, anode fabrication facilities, and reduction cell rooms.

Items yet to be resolved before commercialization of the technology can be considered:

- All of the benefits and achievements described in this report are based on the utilization of a stable, drained, wetted cathode in conjunction with the utilization of a metal inert anode. As a separate project, research was also performed on alternates to the utilization of titanium diboride as a cathode material. The results of this research concluded that high-purity titanium diboride was still the best option for a stable, wetted cathode for utilization in aluminum reduction. During the inert anode development work, commercially available hot-pressed TiB_2 was used for almost all of the testing performed. This material proved unsuitable for the long, sustained operation that will be necessary

before the inert anode technology can be commercialized. Therefore, the most critical development requirement is considered to construct cathodes suitable for long-term usage with the Low Temperature Electrolysis Inert Anode technology.

- In many of the longer runs performed, there was some dissolution of the dense alumina sleeves used for the protection of anode and cathode risers at the bath line. Also, from initial operations of the 5,000 and 1,000 ampere cells, it appeared that the high-alumina castable utilized as cell linings was subject to some dissolution in the bath. Although the alumina content of the cell was kept as closely as possible to saturation or above saturation, local areas of the bath must be below saturation for additional alumina to be dissolved. The bath just exiting the reaction zone is the most likely area that is below saturation in dissolved alumina and this is the area of the preferred location of anode and cathode risers. The second most critical additional development is considered to be alternate materials for the construction of the anode and cathode riser protection. An alternative to this material may be the development of a procedure to selectively freeze a layer of cell bath in this zone.
- During testing in the pilot plant and development line, subtle changes in the characteristics of the feed alumina were observed to have a significant effect on cell performance. In conjunction with the item above, tests to increase the solubility of Bayer process alumina at the normal temperatures and bath compositions of the inert anode need to be performed. If the solubility of alumina can be improved without increasing the general dissolving ability of the bath, then the high density fused alumina may be suitable for the protection of electrical risers. Although less critical than protection of the risers, an increase in the solubility of feed alumina would also improve the performance of the high alumina castable materials as cell liners.
- Additional design and testing is necessary to resolve the best methods to maintain even thermal distribution and cooling with an inert anode cell. The variation of current in an inert anode cell from 50% of capacity to 100% of capacity dramatically increases the amount of heat generated in the cell. The cell must be heavily insulated to sustain the desired temperature at the 50% load capacity rating. An increase in current to 100% results in an increase in heat generated of approximately 553%. $[(V_c - V_d)^2 / R_c]$ where V_c is cell voltage, V_d is alumina decomposition voltage, and R_c is cell resistance.] In the initial design of the 5,000-ampere cell, this issue was addressed by attempts to cool the lining of the cell with air ventilation tubes. Analyses of the data from two limited runs indicated that this was not a viable solution. It appears that a better solution would be to heavily insulate the cell and provide auxiliary

cooling by cooling the anodes and/or cathodes themselves to remove excess heat when the load is changed. Since the anodes are metal with a high heat transfer rate and reasonably machinable, they would appear to be the most likely candidate for alternate cooling options, but this must be built and tested.

- Several anode alloys were tested that yielded promising results in the limited runs of up to 350 hours that could be performed before cathode problems resulted. The ideal anode alloy would result in low rate of metal contamination and a stable resistance over extended periods of operation. These dictates that the corrosion rate of the anode be essentially equal to the rate of oxidation layer growth so a stable, consistent oxidation layer results with a consistent resistance. In several development tests, low metal contamination and stable resistance were demonstrated, but the duration of these tests was less than the 1,000 hours considered necessary to demonstrate anode stability. Additional long term testing of the most promising of the anode alloys will be required to fully develop the best anode alloy.

Potential for retrofit of existing Hall-Herlout cells:

The inert anode roadmap devotes considerable discussion to the retrofit of existing cells with inert anode technology. There were no results obtained during NAT's research and development that were encouraging with respect to retrofit using low temperature electrolysis and metal anodes. The operating temperature of conventional reduction cells is in the range of 950° C. No tests were run on the performance of the Cu-Ni-Fe anodes at temperatures this high, but it is expected that the anode alloy would have considerably less strength and experience more corrosion at temperatures this high. Although higher bath temperatures would greatly increase the solubility of the bath with respect to alumina, it would also increase the dissolution rate of the dense alumina protective sleeves used to protect anode and cathode risers.

The bath ratio of a conventional cell could be modified by the addition of aluminum fluoride to achieve the low temperature bath utilized in NAT's developments, however, this has been attempted by others in prior experiments with the result that freeze layers of the bath on the cathode developed and the cell could not be operated in these temperature ranges. The results of NAT's research indicates that to utilize low temperature electrolysis a wettable, drained cathode is required that is electrically disconnected metal pad.

Summary of conclusions:

- It was demonstrated that high purity aluminum at high current with anodes constructed of inexpensive alloys of copper, nickel and iron can be produced; that these anodes can be fabricated by conventional means of casting, machining and welding; and that standard smelter grade alumina and bath materials can be utilized.
- The potential for reduced energy consumption and significant reduced energy costs were demonstrated.
- The environmental benefits of low temperature bath electrolysis in conjunction with metal anodes were demonstrated.
- Additional research is necessary to provide an acceptable cathode for low temperature inert anode electrolysis; to develop a bath resistant material for electrical connection and cell lining protection; and alternate cooling methods to achieve the full benefits of the potential dynamic range of an inert anode cell.

Patents and applications associated with DOE Contract DE-FC36-98ID13662:

Patent or Serial Number	Date issued or filed	Title:	Associated Grants	Inventor:
6,419,812	7/16/2002	Aluminum Low Temperature Smelting Cell Metal Collection	DOE Grant DE-FC07-98ID13662	Beck, et al
6,419,813	7/16/2002	Cathode Connector for aluminum low temperature Smelting Cell	DOE Grant DE-FC07-98ID13662	Brown et al
6,436,272	8/20/2002	Low Temperature Aluminum Reduction Cell Using Hollow Cathode (CIP of 247,196)	PNNL 320879-AF2, DOE DE-FC07-98ID13662	Brown et al
6,558,525	5/6/2003	Improved Anode for Use in Aluminum Producing Electrolytic Cell	DOE Grant DE-FC07-98ID13662	Bradford et al
6,723,222	4/20/2004	Cu-Ni-Fe Anodes having Improved Microstructure	DOE Grant DE-FC07-98ID13662	Bergsma et al
6,800,191	10/5/2004	Electrolytic Cell for Producing Aluminum employing Planar Anodes	DOE Grant DE-FC07-98ID13662	Barnett et al
6,811,676	11/2/2004	Electrolytic cell for Production of Aluminum from Alumina	DOE Grant DE-FC07-98ID13662	Bradford et al
6,837,982	1/4/2005	Maintaining Molten Salt electrolyte Concentration in Aluminum-Producing Electrolytic Cell	DOE Grant DE-FC07-98ID13662	Barnett et al
6,866,768	3/15/2005	Electrolytic Cell for Production of aluminum from alumina (CIP #195,733)	DOE Grant DE-FC36-98ID13662	Bradford et al
287,029	11/4/2002	Removal of aluminum from a Reduction Cell employing a Hollow Cathode	Grants PNNL #C-320879-AF2, DOE DE-FC07-98ID13662.	Brown
431,403	5/8/2003	Cu-Ni-Fe Anode for use in Aluminum Producing Electrolytic Cell	DOE Grant DE-FC36-98ID13662	Bergsma et al
434,108	12/17/2002	New Electrolytic Cell and Method of Operating Same (Perfected to Serial # 387,602, patent 6,866,768)	DOE Grant DE-FC36-98ID13662	Bradford et al

Publications and Presentations:

Craig W. Brown, "In-Situ Observations of Frozen Electrolyte in Laboratory Reduction Cells," *Light Metals 2003* (TMS, 2003), pp. 293-298 (also presented at the TMS annual meeting.)

Craig Brown, "Next Generation Vertical Electrode Cells", *Journal of the Minerals, Metals and Materials Society* (Volume 53, Number 5, May 2001), pp. 39-42. (also presented at the TMS annual meeting.)

Craig W. Brown, "Laboratory Experiments with Low-Temperature Slurry-Electrolyte Alumina Reduction Cells," *Light Metals 2000* (TMS, 2000), pp. 391-395. (also presented at the TMS annual meeting.)

Inert Anode Metal Life in Low Temperature Aluminum Reduction Process. Presented at Aluminum Industry of the Future Program Annual Program Review 2000, Washington, DC, November 8, 2000; Updated and Presented at OIT Aluminum Portfolio Group Annual Program Review 2001 Lexington, KY, October 17, 2001; Updated and Presented at OIT Aluminum Portfolio Group Annual Program Review 2002, Lexington, KY, December 3, 2002.

Related Publications and Presentations:

Dr. Brown was an invited speaker at the DOE-sponsored Manufacturing Leaders Workshop, Portland, OR, May 1999.

Craig W. Brown, *Journal of the Minerals, Metals and Materials Society* (Volume 50, Number 5, May 1998), pp. 38 - 40. This was also presented at the TMS Annual Meeting, 1998.

Craig W. Brown, "Final Report: Wetted Cathodes for Low-Temperature Aluminum Smelting" (Report DOE/ID-13901, UDSOE Office of Industrial Technologies, 2002).

PATENT CERTIFICATION

Northwest Aluminum Technologies

☐ Interim Certification

Contractor

☒ Final Certification

DE-FC36-98ID13662

DOE Prime and/or Subcontract Nos.

Contractor hereby certifies that:

1. All procedures for identifying and disclosing subject inventions as required by the patent clause of the contract have been followed throughout the reporting period.
2. There were no subcontracts or purchase orders involving research, development, and demonstration except as follows: [State none when applicable.]

None

3. No inventions or discoveries were made or conceived in the course of or under this contract other than the following
(Certification includes ☒ , does not include ☐ all subordinates):
[State none when applicable.]

TITLE

INVENTOR

DATE REPORTED

DOE "S" NO.*

**See attached list
for patent numbers,
titles, and
inventors.**

4. The completion date of this contract is as follows: **03/31/2005**

5. The following period is covered by this certification:

September	17	1998	to	March	31	2005
Month	Day	Year		Month	Day	Year

Contractor

**Northwest Aluminum Technologies
3313 Northwest Second Street
The Dalles, Oregon, 97058**

Signature

06/30/2005

Date of Certification

Address

* Also include Subcontract No. If available

Patents issued and filed under DOE Contract DE-FC36-98ID13662

Patent or filing number	Title	Inventor	Date Reported	DOE "S" No.
6,419,812	Aluminum Low Temperature Smelting Cell Metal Collection	Beck, et al	10/2002	
6,419,813	Cathode Connector for Aluminum Low Temperature Smelting Cell	Brown, et al	10/2002	
6,436,272	Low Temperature Aluminum Reduction Cell Using Hollow Cathodes	Brown, et al	10/2002	
6,558,525	Improved Anode for Use in Aluminum Producing Electrolytic Cell	Bradford, et al	07/2003	
6,723,222	Cu-Ni-Fe Anodes having Improved Micro- structure	Bergsma, et al	07/2004	
6,800,191	Electrolytic Cell for Producing Aluminum employing Planar Anodes	Barnett, et al	01/2005	
6,811,676	Electrolytic cell for Production of Aluminum from Alumina	Bradford, et al	01/2005	
6,837,982	Maintaining Molten Salt Electrolyte Concentration in an Aluminum-producing Electrolytic Cell	Barnett, et al	04/2005	
6,866,768	Electrolytic Cell from Production of Aluminum from Alumina	Bradford, et al	04/2005	
287,029	Removal of Aluminum from a Reduction Cell employing a Hollow Cathode	Brown		
431,403	Cu-Ni-Fe Anode for Use in Aluminum- Producing Electrolytic Cell	Bergsma, et al		
434,108	New Electrolytic Cell and Method of Operating Same (perfected to 6,866,768)	Bradford, et al		

June 27, 2005

Mr. Tom Anderson
Intellectual Property Law Division
U. S. Department of Energy
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439

Re: DOE Grant DE-FC36-98ID13662

Dear Mr. Anderson:

In accordance with our telephone conversation on June 20, 2005 regarding patents acquired due to work under the referenced grant, as you requested I am forwarding a copy of the Patent Certification Form DOE F 2050.11 and copies of the patents applied for and granted as listed on the form.

Attached to the form is a listing of the patents. Also on the listing are applications for patents not yet granted. One of these has been perfected into one of the patents listed as granted. The other two applications may or may not be continued to patent issuance.

Copies of the nine patents granted are also attached.

Sincerely yours,

A handwritten signature in cursive script that reads "Donald R. Bradford".

Donald R. Bradford
For Northwest Aluminum Technologies

**U.S. DEPARTMENT OF ENERGY
GOLDEN FIELD OFFICE**

PROPERTY INVENTORY CERTIFICATE-ASSISTANCE

Grant/Cooperative Agreement No. DE-FC36-98ID13662	Grantee/Recipient Northwest Aluminum Technologies		
Based on the Grantee/Recipient records, and in accordance with the Property Standards set forth in 10 CFR 600.130 through 600.137 (600.230-600.233 for States), all real and personal property provided by, or partially or wholly funded by, DOE, and now in the custody of the Grantee/Recipient is listed and accounted for below.			
I. REAL PROPERTY (Real estate)(10 CFR 600.132/600.232) A. <u>Federally-Owned:</u> ☒ NO ☐ YES (If yes, attach list the property) B. <u>Acquired With Project Funds:</u> ☒ NO ☐ YES (If yes, list below and complete C) C. ☐ The property will continue to be used for the purposes authorized by the award. ☐ The property is no longer needed and DOE disposition instructions are requested. ☐ The property is no longer needed for the purposes of the award, and DOE approval is requested to use the property for project(s) listed below:			
II. NONEXPENDABLE PERSONAL PROPERTY (Equipment)(10 CFR 600.134/600.232) A. <u>Federally-Owned:</u> ☒ NO ☐ YES (If yes, attach list of property) B. <u>Acquired With Project Funds:</u> ☐ NO ☒ YES C. <u>Acquired With Project Funds and Exempt:</u> ☒ NO ☐ YES (If yes, explain why and attach list) D. <u>Acquired With Project Funds and NOT Exempt:</u> Property in inventory at a unit fair market value of \$5000 or more: ☐ NO ☒ YES (If yes, complete (1)-(3) below) (1) ☒ Property will continue to be used for the purposes authorized by the award. (2) ☐ Property is no longer needed for Project, and shall be used in the following federally-sponsored activity/activities: (3) ☐ Property is no longer needed for Project or other federal activities, and: ☐ Grantee/Recipient requests DOE disposition instructions. ☐ Grantee/Recipient wishes to retain the property and: Fair Market Value of the property is estimated at \$58,298 Basis of estimate: Depreciation schedules on individual items shown on the attached equipment list			
III. EXPENDABLE PERSONAL PROPERTY (10 CFR 600.135/600.233) A. ☐ There is residual inventory exceeding \$5000 in aggregate fair market value. (If checked, continue.) B. ☐ The property will be used on other federally-sponsored activities. C. ☐ The property will be retained for use on other nonfederally-sponsored activities. (If checked, complete D.) D. The Aggregate Fair Market Value of the property is Basis of estimate of value is			
Name: Donald R. Bradford	Signature: 	Title: Technical Manager	Date: 06/30/2005

To be completed by the Government:

Project Officer Signature:	Date:
Recommended Property Disposition:	
Property Officer Signature:	Date:

DE-FC36-98ID13662

**Non-Expendable Personal Property List and Basis for Valuation
Attachment to DOE Form GO-PF13a, Property Inventory Certificate-Assistance**

Equipment Item:	Date Acquired	Acquisition Cost	Depreciation Life	Current Value (04/01/2005)
Sorenson 10-2000 Rectifier (1 of 3)	11/2001	\$10,560	7 years	\$5,531
Sorenson 10-2000 Rectifier (2 of 3)	11/2001	\$10,560	7 years	\$5,531
Sorenson 10-2000 Rectifier (3 of 3)	12/2001	\$10,560	7 years	\$5,657
High Speed 20 inch Lathe	07/2002	\$12,900	10 years	\$9,460
Kent 3-axis Milling Machine	11/2002	\$20,500	10 years	\$15,172
Jetline Equipment Inert Gas Welding Station	12/2002	\$24,974	7 years	\$16,947

Current Value Total: \$58,298