# Electrolytic Production of Sodium Perchlorate Using Lead Dioxide Anodes

Joseph C. Schumacher, David R. Stern, and Paul R. Graham

*American Potash & Chemical Corporation, Whittier, California*

## ABSTRACT

Lead dioxide was investigated as an anode substitute for platinum in the production of sodium perchlorate. Rod shaped deposits were prepared on nickel and platinum clad tantalum wires. The plate was dense, heavy, metallic-like in appearance and not too fragile for ordinary handling. The first phase of experimentation was performed in small laboratory cells to determine approximate electrolyses data. Larger bench-scale production cells were also run simulating plant operating conditions. Lead dioxide anodes produce sodium perchlorate at high cumulative current efficiencies. One lead dioxide anode was used in cell operation for 3,000 hr. Cumulative current efficiency for a given anodic current density is a function of the cathode material, cathodic current density, and the additive used. Perchlorate can be produced using nickel, copper, stainless steel, and carbon steel cathodes. Energy requirements, under identical experimental conditions, indicate that stainless steel and nickel are the best cathode materials. A current efficiency of 91.5% was obtained with a stainless cathode at anodic and cathodic current densities of 15.5 amp/dm$^2$ and of 7.25 amp/dm$^2$, respectively. No unusual metallic contamination could be detected in the ammonium perchlorate prepared from the sodium perchlorate.

Increased demand for $NaClO_4$ as an intermediate for the production of ammonium and potassium perchlorates resulted in a search for a replacement for the Pt anode. Previous investigations have shown that $PbO_2$ might be a satisfactory substitute for Pt. Lead dioxide electrodes in various sizes and shapes may be prepared from suitable electrolytic baths (1-4). The rod-shaped electrodes used in these experiments were prepared by plating $PbO_2$ on Ni and Pt clad Ta wires. Platinum clad Ta as a conductor on which to deposit the $PbO_2$ had the advantage of being corrosion resistant to the $HNO_3$ liberated during electrolysis from the $Pb(NO_3)_2$ electrolyte. The $PbO_2$ deposit is dense, heavy, and metallic in appearance. Perchlorates can be produced on $PbO_2$ deposits from 8-10 mm thick (4). Thin deposits are fragile and erode easily during electrolysis. When a thickness of at least 20 mm is obtained, the electrode is not too fragile for ordinary handling and erosion is not significant.

The over-all chemical equation for the electrochemical oxidation of chlorate to perchlorate has been reported by other investigators (5-9).

The investigation was divided into two phases. The first dealt with exploratory experiments in small laboratory cells designed to determine feasibility, to approximate electrolyses data, and to evaluate different cathodes with small $PbO_2$ anodes. On the basis of these experiments, larger cells were operated simulating actual plant conditions. The first phase of the investigation is referred to as laboratory cell experimentation and the latter phase as bench-scale production.

Three methods for measuring current efficiencies have been used by other investigators and were used in this study. They were:

*Gas collection.*—If a standard coulombic cell with Pt electrodes containing a 5% NaOH electrolyte is connected in series with a perchlorate cell, the ratio of gas volumes in the coulombic cell to that of the

perchlorate is 3:2. Thus, the gas volumes from the coulombic and perchlorate cells give an approximate measure of the instantaneous current efficiency. This may not be too accurate if there are appreciable side reactions.

*Chlorate depletion.*—If side reactions are negligible, then the $NaClO_3$ disappearing can be used as an approximation to current efficiency.

*Perchlorate determination.*—This measurement is the most accurate determination of current efficiency, but necessitates a time consuming perchlorate analysis. Moreover, this is a cumulative and not an instantaneous current efficiency.

Gas collection and chlorate depletion are easily and rapidly obtained and may indicate the trend of a variable. Gas collection was utilized for the small laboratory cells, recognizing that it was only an approximation, which would be checked by direct analyses later on the bench-scale production cell.

Data obtained by analyses on the bench-scale cell indicate that inefficiencies due to side reactions are of small magnitude with some cathodes and that the current efficiency measurement used for the laboratory cells has some validity.

## Laboratory Cell

*Cell construction.*—Laboratory cells were constructed of ⅛ in. Lucite. They were cylindrical in shape, 2½ in. I.D. x 5 in. high. The electrodes, a thermometer, and a ¼ in. diameter x 1½ in. gas outlet tube were sealed through the cell cover. A rubber gasket was fitted to a ½ in. flange around the top of the cells. Wing nuts through the flange secured the cover, creating a gas-tight fitting.

Evolved gas was directed to 50 ml burets. Volumes were measured by the displacement of water in the burets.

Electrolyte levels in both cells were maintained 1 in. from the top; this gave a small equal volume. Electrolysis time, while the gases were being collected, was short. Since a ratio of volumes was utilized, no corrections for pressure and temperature were necessary; it was assumed that the burets remained under identical conditions, even though volumes of different magnitude were involved.

Lead dioxide was employed as the anode in the laboratory cell except for the initial experiments. A Pt anode was used in these experiments to establish reference data. Two cathodes connected in parallel were used. The initial concentration of the electrolyte was approximately 500 g/1 of reagent grade $NaClO_3$ with various additives. New electrolyte was used for each series of experiments.

Temperatures of both cells were controlled with external water cooling within 5°C.

*Experimental procedure.*—The coulombic and laboratory cell were connected in series to a Se rectifier. Current and voltage across the laboratory cell were measured during electrolysis. These cells were operated until the coulombic cell had evolved 50 ml of gas. Comparison of this volume to that evolved from the laboratory cell gave the current efficiency. Each experiment was made under a controlled current density. The pH of the electrolyte was controlled within a given range and was adjusted with HCl or NaOH.

The cells were operated a sufficient length of time after reaching thermal equilibrium to purge the dead air space. During this time gas was evolved to the atmosphere. When a steady rate of evolution existed, the gas was collected in the burets and data recorded during the collection of the gas samples. Current was varied from 1.33 to 5.30 amp, while the voltage across the laboratory perchlorate cell covered the range of 4.0-6.1 v. A temperature range of 20°-40°C was investigated.

### Experimental Results

To establish reference data, the initial experiments utilized a Pt anode in the laboratory perchlorate cell. After this, experiments were conducted using $PbO_2$ as the anode with Cu, carbon steel, Ni, and stainless steel as the cathodes. Variables observed were current efficiency, current density, cell temperature, electrolyte concentration, pH, cathode material, and additives. Some of these data are presented in Table I. The most satisfactory values of cell operating conditions were selected from these data for subsequent verification in the larger bench-scale production cell.

Table I. Experimental results of laboratory perchlorate cells

| Material | | Anodic current density (amp/dm²) | Voltage (volts) | Current (amp) | Temp range (°C) | pH | Initial concentration (g/l) | | | Current* efficiency (%) |
| Anode | Cathode | | | | | | Electrolyte | Additive | | |
| | | | | | | | NaClO₃ | NaF | Na₂Cr₂O₇ | |
|---|---|---|---|---|---|---|---|---|---|---|
| Pt | Carbon steel | 31.0 | 5.2 | 2.90 | 20-25 | 6.0 | 484.5 | — | 5 | 92.8 |
| PbO₂ | Carbon steel | 15.5 | 4.6 | 2.46 | 30-35 | 6.5 | 484.5 | — | 5 | 37.7† |
| PbO₂ | Copper | 15.5 | 4.4 | 4.71 | 30-35 | 6.0 | 484.5 | — | 5 | 36.3 |
| PbO₂ | Copper | 15.5 | 5.0 | 1.47 | 35-40 | 6.5 | 500.0 | 0.5 | — | 92.4 |
| PbO₂ | Nickel | 7.25 | 4.0 | 1.33 | 35-40 | 6.5 | 500.6 | 0.5 | — | 93.5 |
| PbO₂ | Nickel | 15.5 | 5.0 | 1.47 | 35-40 | 6.5 | 493.5 | — | — | 84.8 |
| PbO₂ | Nickel | 15.5 | 5.0 | 1.47 | 35-40 | 6.5 | 493.5 | 0.5 | — | 92.3 |
| PbO₂ | Nickel | 15.5 | 5.3 | 1.47 | 35-40 | 6.5 | 493.5 | 1.5 | — | 92.7 |
| PbO₂ | Nickel | 15.5 | 5.2 | 1.47 | 35-40 | 6.5 | 493.5 | Saturated | — | 93.0 |
| PbO₂ | Nickel | 15.5 | 4.9 | 2.65 | 35-40 | 6.5 | 500.6 | 0.5 | — | 93.7 |
| PbO₂ | Nickel | 23.25 | 5.8 | 2.21 | 35-40 | 6.5 | 493.5 | 0.5 | — | 92.7 |
| PbO₂ | Stainless steel (302) | 31.0 | 6.1 | 5.30 | 25-30 | 6.5 | 495.2 | 0.5 | — | 97.5† |

* Approximate instantaneous current efficiency based on gas collection technique.
† Discoloration of evolved cell gases during electrolysis indicated that side reactions were taking place.

*Conclusions.*—Examination of the data in Table I indicates that the following conclusions may be made:

1. Sodium perchlorate can be made by electrolysis using a $PbO_2$ anode with Cu, carbon steel, Ni, or stainless steel cathodes.

2. Current efficiencies appear to be higher with Ni, stainless steel, and Cu cathodes than with carbon steel.

3. Data obtained with carbon steel are not conclusive because of side reactions.

4. Sodium fluoride appears to be a better additive than sodium dichromate. The minimum effective NaF concentration is 0.5 g/l.

5. Data obtained with a $PbO_2$ anode, Ni cathodes, and a NaF additive indicate that the current efficiency is practically independent of current density, temperature, and pH in the range of variables investigated. An instantaneous current efficiency of 93.7% was obtained at an anodic current density of 15.5 amp/dm$^2$.

6. Lower voltages appear to be possible using $PbO_2$ anodes.

## Bench-Scale Production Cell

The first phase of the investigation had set up sufficient design criteria to proceed with the construction of a larger unit which could be operated semicontinuously and for longer periods of time. All the variables could be evaluated based on the current efficiency, which could be determined by a direct chemical analysis. In order to proceed with this unit, larger $PbO_2$ anodes were made.

*Bench-scale cell construction.*—The cell was a 4-liter resin reaction kettle with a bottom outlet (Fig. 1). Current was provided by a Se rectifier
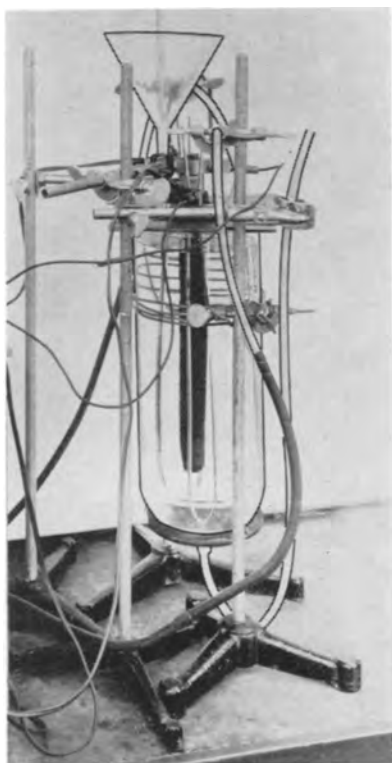
and voltages and current measurements obtained. Temperature was controlled by circulating water through a glass coil immersed in the electrolyte. When pH control was necessary, 18% HCl was added.

The anode consisted of a rod-shaped, rough surfaced $PbO_2$ electrode and was immersed in solution so that, at a current of 26 amp, the anodic current density was 15.5 amp/dm$^2$. This value was maintained constant in all experiments. It proved to be the best value obtained in the smaller laboratory cells and simulates approximate plant operating conditions. Cathodes were U-shaped metal rods of varying diameters by 15 in. in length. The anode, cathodes, cooling coil, and thermometer were inserted through the top of the cell into the electrolyte. An electrical connection was made at the top of the anode with a Ag-plated Cu clamp. Cathodes were on 3 in. center to center spacing, with the anode centered between them or 1½ in. from the cathodes. Figure 2 is a picture of a typical $PbO_2$ anode with the cathodes used.

Electrolyte could be removed from the bottom of the cell and returned to the top to insure adequate mixing.

*Experimental procedure.*—At the start, the cell was filled with 4 liters of solution containing approximately 500 g/l $NaClO_3$ plus the additive. The pH and temperature were recorded. A value of 6.9 was considered to be the maximum limiting pH while the temperature was controlled within the range of 30°-45°C. Current was adjusted to the desired anodic current density, and voltage noted.

Electrolyte was removed during electrolysis from the bottom of the cell and returned through the top. About 2 liters were removed in from 2 to 3 min in 500 ml increments. This served to keep the electrolyte well circulated and was repeated every half hour. After recirculation was completed, a 100 ml sample was secured and the pH measured. This sample was returned to the cell and the pH adjusted, if necessary.

A 15 ml sample was taken for chemical analysis every 2 hr after recirculation. Then 15 ml of make-up solution were added to maintain constant volume.

The addition of make-up solution is important, since no drastic concentration changes in the electrolyte could be introduced. During the initial phases of the experiment the make-up solution contained 300 g/l $NaClO_3$. This solution was used until the concentration of the electrolyte in the cell dropped to 150
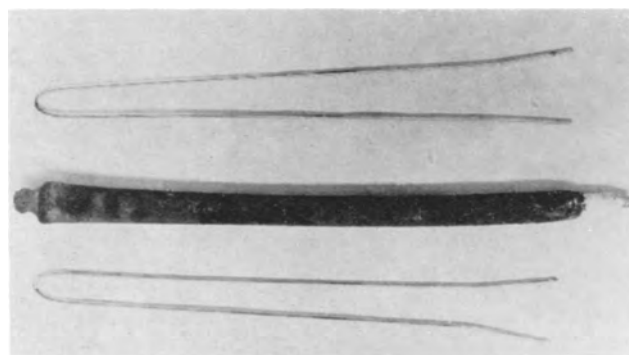


Fig 1. Internal arrangement of bench-scale production cell
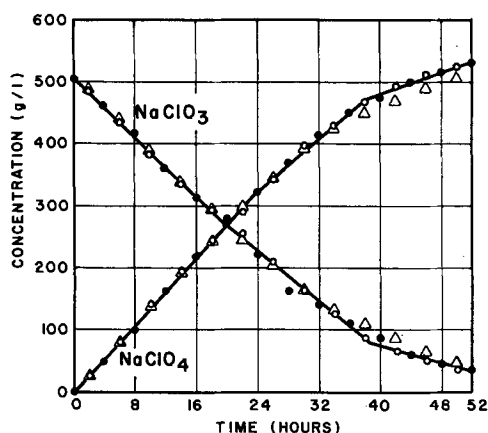


Fig. 2. Typical $PbO_2$ anode-nickel cathodes

Fig. 3. Effect of PbO₂ conductor wire. Electrolysis conditions: anodic C. D. = 15.5 amp/dm²; cathodic C. D. = 7.25 amp/dm²; temp. range = 30°-45°C; cell voltage = 5.2-5.3 v; pH = 5.2-5.7; NaF conc. = 0.5 g/l. Anode: solid circle, PbO₂ plated on Ni wire; open circle, PbO₂ plated on Pt clad Ta; open triangle, PbO₂ plated on Ni wire.
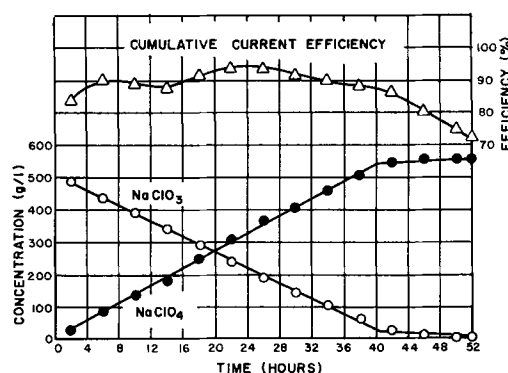


Fig. 4. Effect of nickel cathodes on cumulative current efficiency. Electrolysis conditions: anodic C. D. = 15.5 amp/dm²; cathodic C. D. = 7.25 amp/dm²; temp. range = 35°-45°C; cell voltage = 5.0 v; pH = 5.3; NaF conc. = 0.5 g/l; anode: rough surface rod-shaped, 2.06 cm dia. x 45.72 cm long; cathode: two U-shaped Ni rods, 0.95 cm dia. x 38.10 cm long.
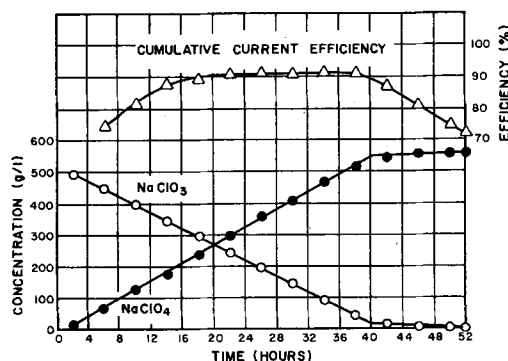
g/l of chlorate. From this point, make-up solution of 150 g/l was added until the concentration dropped to 100 g/l. Then solution adjusted to the chlorate composition of the electrolyte was added until the completion of the experiment.

Every 2 hr a 15 ml sample was analyzed immediately for its sodium chloride and chlorate concentrations. Since the perchlorate determination was time consuming, samples were taken only every 4 hr for analyses.

Experiments were carried out for 52 hr continuously, except when side reactions or chlorate analyses indicated that the obtained efficiencies were too low.

### Experimental Results

Two different PbO₂ anodes were used in the experiments with the bench-scale production cell. One



Fig. 5. Effect of stainless steel cathodes on cumulative current efficiency. Electrolysis conditions: anodic C. D. = 15.5 amp/dm²; cathodic C. D. = 7.25 amp/dm²; temp. range = 35°-45°C; cell voltage = 4.75 v; pH = 5.7; NaF conc. = 0.5 g/l; anode: rough surface rod-shaped, 2.06 cm dia. x 45.72 cm long; cathode: two U-shaped stainless steel (302) rods, 0.95 cm dia. x 38.10 cm long.

**Table II. Experimental results of bench-scale production cells**

| Cathode | Cathode current density (amp/dm²) | Additive | Voltage (volts) | Current[a] (amp) | Time, (hr) | Kw-Hr | Final[b] concentration (g/l) NaClO₄ | NaClO₃ | Cumulative current efficiency (%) | Unit energy[c] (kw-hr/lb) |
|---|---|---|---|---|---|---|---|---|---|---|
| Nickel | 21.4 | NaF[d] | 5.1 | 26.0 | 41.6 | 5.51 | 510 | 50 | 83.0 | 1.23 |
| Nickel | 21.4 | NaF and Na₂Cr₂O₇[e] | 5.3 | 26.0 | 52.0 | 7.16 | 240 | 280 | 31.1 | 3.38 |
| Nickel | 7.25 | NaF | 5.0 | 26.0 | 38.6 | 5.02 | 514 | 50 | 88.2 | 1.11 |
| Stainless steel (302) | 21.4 | NaF | 5.2 | 26.0 | 49.2 | 6.52 | 493 | 50 | 68.0 | 1.50 |
| Stainless steel (302) | 7.25 | NaF | 4.75 | 26.0 | 37.6 | 4.64 | 505 | 50 | 91.5 | 1.04 |
| Stainless steel (302) | 7.25 | NaF and Na₂Cr₂O₇[f] | 4.75 | 26.0 | 24.0 | 2.96 | 235.5 | 287.6 | 66.0 | 1.43 |
| Copper | 21.4 | NaF | 5.7 | 26.0 | 42.8 | 6.36 | 492 | 50 | 78.5 | 1.47 |
| Carbon steel | 21.4 | NaF | 5.1 | 26.0 | 52.0 | 6.89 | 264 | 214 | 34.2 | 2.96 |
| Carbon steel | 14.1 | Na₂Cr₂O₇[g] | 4.9 | 26.0 | 48.0 | 6.13 | 68 | 445 | 9.9 | 10.23 |

[a] Anodic current density = 15.5 amp/dm².
[b] Volume = 4 liters.
[c] Commercial production requires 1.5-1.9 kw-hr/lb at 6.2-6.8 v, and anodic current densities of 31.1-52 amp/dm² (11).
[d] NaF as an additive = 0.5 g/l concentration.
[e] Na₂Cr₂O₇ concentration = 0.5 g/l.
[f] Na₂Cr₂O₇ concentration = 0.003 g/l.
[g] Na₂Cr₂O₇ concentration = 5.1 g/l.

Table III. Spectrographic analyses of unpurified ammonium perchlorate

| Cathode material | Nickel | Stainless steel (302) | Copper |
|---|---|---|---|
| Major constituent* ** | Sodium | Sodium | Sodium |
| Intermediate constituent | Potassium | Potassium | Potassium |
| Minor constituent | Approximate % | Approximate % | Approximate % |
| Calcium | 0.10 | 0.10 | 0.10 |
| Aluminum | 0.05 | 0.05 | 0.01 |
| Iron | 0.05 | 0.01 | 0.005 |
| Magnesium | 0.01 | None found | None found |
| Silicon | 0.01 | 0.01 | None found |
| Barium | 0.01 | 0.01 | 0.01 |
| Chromium | 0.005 | 0.001 | 0.001 |
| Copper | 0.005 | 0.01 | 0.005 |
| Vanadium | 0.005 | 0.001 | 0.001 |
| Nickel | 0.005 | None found | None found |
| Manganese | 0.001 | None found | None found |
| Lead | 0.001 | Trace | Trace |
| Wt of Ash (g) | 1.62 | 1.39 | 3.03 |

\* Mother liquor hold-up.
\*\* Based on spectrographic analyses of ash.

anode consisted of $PbO_2$ plated on Pt clad Ta and the other was plated on Ni wire. Experimental results obtained when $PbO_2$ is plated on these two different conductors are presented in Fig. 3. When sodium dichromate was used as an additive, a thin yellow deposit was formed on the surface of the $PbO_2$ anode. Cathodes were constructed of Ni, Cu, carbon steel, and 302 stainless steel. The effects of cathodic current density and additives were also investigated. Some experimental results are presented in Table II.

A typical result, using Ni cathodes, illustrating the change in electrolyte concentration as a function of time and the cumulative current efficiency is presented in Fig. 4. Figure 5 presents results with stainless steel cathodes.

Sodium perchlorate produced in these bench-scale experiments was converted to ammonium perchlorate to determine purity and for evaluation purposes. Only the first crop of unwashed crystals was selected for chemical and spectrographic analyses. Table III presents spectrographic data on the ammonium perchlorate prepared, and indicates that no unusual quantity of metallic impurities was introduced into the perchlorate.

*Conclusions.*—The following conclusions may be reached from the experimentation, utilizing $PbO_2$ anodes as a substitute for Pt in the production of sodium perchlorate:

1. Lead dioxide anodes produce sodium perchlorate at high cumulative current efficiencies.

2. The cumulative current efficiency for a given anodic current density is a function of chlorate concentration, the cathode material, the cathodic current density, and the additive used.

3. The wire on which the $PbO_2$ was plated for an anode appears to have no effect on the production of sodium perchlorate.

4. Sodium perchlorate can be produced using cathodes of Ni, Cu, stainless steel, and carbon steel. However, efficiencies with carbon steel are very low.

5. Sodium dichromate has a detrimental effect on the current efficiency by forming a thin deposit on the surface of the $PbO_2$ anode.

6. Decreasing the cathodic current density increased the current efficiency when utilizing Ni and stainless steel cathodes.

7. One $PbO_2$ anode was used in the cell operation for 3,000 hr.

8. Ammonium perchlorate was prepared from the sodium perchlorate produced in these experiments. No unusual metallic contamination was present and the ammonium perchlorate meets present commercial specifications.

9. Comparison of energy requirements calculated for identical experimental conditions indicates that Ni and stainless steel are the best cathode materials and that $PbO_2$ offers energy advantages over Pt as an anode.

10. Energy results of 1.04 kw-hr/lb of sodium perchlorate with a cumulative current efficiency of 91.5% were obtained. These results were attained with stainless steel cathodes at a cathodic current density of 7.25 amp/dm² and a final sodium chlorate concentration of 50 g/l.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1958 JOURNAL.

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