# Continuous Electrodialysis Treatment of Electroless Nickel Field Results

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Electrodialysis has become an important method to extend the bath life of electroless nickel. Recently, a new continuous treatment method has been developed and installed in a plating shop for tests. The results of these tests provide insight into the importance of the operation parameters that determine the overall efficiency of the treatment. This paper will discuss the use of a Design of Experiments technique to help optimize the numerous parameters that affect the treatment results.

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## Introduction

An electroless nickel process, as well as other electroless plating processes, has a limited useful bath lifetime, after which the bath must be discarded. During this lifetime the plating and deposit properties tend to change, especially toward the end of the bath life, so that the plating technician cannot process a particular part exactly the same way each time, and cannot expect exactly the same deposit each time.

There have been a number of approaches developed and tested to extend the life of the electroless nickel process and reduce the waste produced [1]. Electrodialysis is one of these techniques [2,3,4,5,6,7]. We recently discussed several strategies [8] that have been used as the electrodialysis (ED) process has developed.

A. Originally the ED process was used with electroless nickel (EN) as a batch process. Once the EN plating bath had reached the end of it's useful life the bath was transferred to the ED unit, processed, and rebuilt.
B. The second strategy is the frequent batch process. The EN process bath is used for a day (one or two shifts perhaps) and then the ED unit is turned on to treat the bath during the night.
C. The third strategy is the Continuous Low Temperature process. Since many of the ED membranes in use today are limited to temperatures of 40°C or less, the ED unit is designed to cool the plating bath, treat it by electrodialysis, and return the treated bath continuously during production.
D. The fourth method is to continuously treat the EN solution at high temperature. Membranes capable of tolerating high temperature have been applied [9] to the ED of EN. The bath does not have to be cooled significantly (saving energy costs) and is fed through a heat exchanger into the ED unit that operates at 70-80°C. The treated EN solution is fed back through the other side of the same heat exchanger and back into the plating tank.

The results of field tests of the third strategy will be discussed in this paper. Because the ED system has many variable parameters and testing time was short, a Design of Experiments (DOE) test series was developed to determine the optimum operating conditions. The Continuous Low Temperature ED for EN method (10) will be compared with normal EN processing and also with using the Bleed and Feed technique on the EN bath. The EN process used for these tests is a specially designed process that operates at 3 g/L of nickel metal ions rather than the traditional 6 g/L.

## Low Metal Electroless Nickel

The traditional EN bath operates at about 6 g/L (or more) of nickel metal ions and about 30 g/L (or more) of sodium hypophosphite. In order to lower costs of the processing and to reduce waste, a dilute EN process solution has been developed that operates at 3 g/L of nickel metal ions and 20 g/L of sodium hypophosphite. The advantages of this approach are:

1. Drag-out losses of nickel are cut in half and sodium hypophosphite are cut by a third.
2. Wasted nickel metal at the end of the bath life is also cut in half.
3. There is no loss of plating rate.

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4. There is no loss in deposit brightness.
5. The electroless nickel deposit properties remain identical to those obtained using traditional bath.

It should be pointed out that since the bath is operated at 3 g/L of nickel metal, the term “metal turn over (MTO)” refers here to the addition of 3 g/L of nickel back into the plating tank during operation.

**Bleed and Feed Operation**

The dilute bath described above has been successfully used in a number of commercial plating shops. Some shops found that, while the bath could be used longer, it was more practical to operate the bath to about 12-16 MTO (equivalent to 6-8 MTO using traditional methods). A bath operating at 12 MTO runs well and the deposit properties are as desired, but an older bath begins to fall off.

With this in mind, a Bleed and Feed operation was developed in which a bath that has reached the age of 12 MTO would have 1/6$^{th}$ of the plating bath removed. The equivalent of 1/6$^{th}$ of the volume of fresh makeup would then be added to the tank. After the bath operates another 2 MTO another 1/6$^{th}$ of the bath is again removed and replaced with fresh makeup. This method is continued and the entire bath is never dumped (baring accidents). The results of the method are as follows:

1. The bath remains constant at 10-12 MTO.
2. The volume of waste is identical to throwing the bath away every 12 MTO.
3. The amount of chemicals is identical to throwing the bath away every 12 MTO.
4. The deposition and deposit properties (plating rate, brightness, hardness, % phosphorous, etc) remain the same from day to day.
5. Overall costs remain identical to disposing of the bath every 12 MTO.

A plating shop located in France, that uses this Bleed and Feed strategy, agreed to test the Continuous Low Temperature ED for EN unit. This plating shop uses automatic controllers for each of the production plating tanks.

**Low Temperature Continuous Electrodialysis**

As previously described [8] the Low Temperature Continuous ED unit* (Fig.1) consists of two processing tanks, C1 and C2. The EN solution from the processing tank is passed through a heat exchanger and then a chiller to cool the solution to about 40°C and fed into tank C1. The solution in C1 and C2 is pumped through the ED membrane stack continuously. The electric potential applied across the ED stack causes ions to be transported across the membranes from the solution in C1 into the solution in tank C2. Tank C2 contains the waste salts that have been transferred through the ED membrane stack.

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* EDEN® System, Pure Cycle Environmental LLC, North Haven, CT

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When the ED process starts up, the solution in tank C2 is just water with a little salt to provide some conductivity. However, as processing continues the solution in C2 builds up with salts. The ED unit is designed to monitor the conductivity of the solution in C2. Once the conductivity reaches a set point the unit pumps out about 1/3rd of the solution into a waste container.

The ED unit also has a trigger that is set off if the volume of the C2 tank reaches a maximum. This trigger causes a pump to transfer a portion of the C2 tank into the waste container if necessary. This volume trigger is necessary because, as the solution in C2 becomes more concentrated, natural osmosis begins to transfer water through the membrane stack causing the volume in C2 to rise quickly. This osmotic effect also became an important design item as the ED unit was tested.

As the testing of the ED unit was planned, we determined that there were five control parameters available to be varied. While other parameters might be important we determined that we could not adequately control them. The flow diagram of the unit is shown in Fig. 1. The parameters are:

1. Orthophosphite in the plating bath. The ED unit cannot really differentiate between orthophosphite and hypophosphite because these ions are very similar. However, ED is sensitive to concentration differences. A material that is present in high concentration will transfer preferentially to a material that is present in low concentration. Thus, the concentration of the orthophosphite in the plating bath is an important variable and can be monitored by conductivity. The conductivity of the plating bath as it varies with orthophosphite concentration is shown in Fig. 2.
2. Orthophosphite in the waste tank C2. The amount of orthophosphite in tank C2 is monitored by the ED unit as conductivity. The conductivity set point on the ED unit determines how frequently a portion of the C2 solution is pumped into a waste tote. The conductivity of the solution in tank C2 as it varies with orthophosphite concentration is shown in Fig. 3.
3. Current. The electrical current flow through the ED membrane stack determines the quantity of materials that are pushed through the stack from C1 to C2.
4. Pressure difference. The pressure difference between the solutions flowing through the two chambers of the ED stack can modify the osmotic flow of water through the stack. However, the stack can only tolerate a small pressure difference across the membranes.
5. Bath flow between the plating process tank and the ED unit tank C1. The solution in C1 should be as close as possible to that in the plating process tank. The flow between the process tank and C1 helps to determine this, however the flow cannot be too high because this can raise the temperature of the ED unit above the 40°C temperature limit of the ED stack membranes.

These five variables were used to design a DOE set of experiments.

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### Goals

There were three goals that had to be met for the ED test to be considered successful.

1. The total waste volume generated had to be less than that obtained during normal operation and during Bleed and Feed operation.
2. The ED unit needed to keep the plating bath at steady state during production.
3. Losses of valuable chemicals needed to be at least comparable (ideally less) to normal or Bleed and Feed operation.

### Design of Experiments

When a process that needs to be optimized has a large number of variables, a Design of Experiment (DOE) strategy can be used to provide guidance for this optimization with a small number of experiments [10]. It is not within the scope of this paper to discuss the DOE method in detail. However, with the five variables mentioned above it becomes evident that eight tests must be run. Table I lists the variables and values that were chosen after preliminary tests and extensive discussions amongst the people involved in the experiments.

**Table I DOE parameters for Continuous Low Temperature ED**

| **Test** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **X1** | **X2** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ortho in Bath (g/L)** | 90-110 | 90-110 | 140-160 | 140-160 | 90-110 | 90-110 | 140-160 | 140-160 | 150-190 | 120-160 |
| **Ortho in C2 (g/L)** | 70-90 | 70-90 | 70-90 | 70-90 | 140-160 | 140-160 | 140-160 | 140-160 | 90-140 | 200-250 |
| **Current (amps)** | 15 | 25 | 25 | 15 | 15 | 25 | 25 | 15 | 18 | 25 |
| **Pressure Difference (PSI)** | 1 | 2 | 2 | 1 | 2 | 1 | 1 | 2 | 1.5 | 1.5 |
| **Flow (L/min)** | 0.8 | 1.5 | 0.8 | 1.5 | 0.8 | 1.5 | 0.8 | 1.5 | 1.5 | 1.5 |
| **Hours of ED** | 31 | 20 | 36 | 24 | 42 | 29 | 8.5 | 31 | 164 | 171 |

From the tests four values were measured: Waste volume per MTO, Nickel % Inefficiency (the percent of nickel lost), hypophosphite % inefficiency (the percent of hypophosphite lost), and orthophosphite % efficiency (the percentage of orthophosphite that is removed). Ideally the amounts of nickel and hypophosphite should be low and all of the orthophospite generated during a day of operation should be removed during that day by the ED unit. Table II lists the data collected for the eight tests. The table also includes two “optimization tests” that were suggested by the data.


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**Table II Results of DOE Tests**

| Test | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | X1 | X2 |
|---|---|---|---|---|---|---|---|---|---|---|
| **ED Time (hrs)** | 30.3 | 19.8 | 35.5 | 23.8 | 41.5 | 28.8 | 8.5 | 30.7 | 163.5 | 170.5 |
| **MTO** | 2. | 2.5 | 3.9 | 1.9 | 1.8 | 3.0 | 2.6 | 2.8 | 11.4 | 10.1 |
| **MTO/24hr** | 1.9 | 2.7 | 3.4 | 1.8 | 1.0 | 2.3 | 6.8 | 2.0 | 1.7 | 1.4 |
| **Waste per MTO (L)** | 137 | 65 | 259 | 179 | 66 | 121 | 61 | 36 | 183 | 150 |
| **Ni %** | 0.57 | 0.34 | 0.40 | 0.29 | 0.13 | 0.64 | 0.29 | 0.12 | 0.43 | 0.84 |
| **Hypo %** | 9.5 | 5.8 | 5.3 | 9.2 | 4.6 | 11.6 | 5.4 | 3.3 | 8.2 | 16.4 |
| **Ortho %** | 47 | 30 | 53 | 68 | 19 | 61 | 45 | 18 | 72 | 117 |

Note: Error between theoretical and measured values of hypophosphite and orthophospite was about 10%

The results from these eight experiments proved difficult to interpret because, due to production demands at the shop, the experiments were not run under similar conditions. For example, most of the experiments took 20-40 hours to use the bath to about 2 MTO. In addition an examination of the complete data shows that none of the experiments managed to maintain the bath at steady state. However, during experiment 7 the bath was used to 2.6 MTO in just 8.5 hours due to very heavy loading during that workday. The ED unit managed to keep up fairly well that day, even though the orthophosphite efficiency seems low at 45%. Due to factors like this the calculations provided by the DOE computer program resulted in very large undetermined effects caused by factors that could not be controlled in the experiments, like production loading. However, the DOE calculations did provide important data that showed the effect and the magnitude of the effect of each variable. This data could be used to determine which direction was helpful in attaining the goals and which direction was harmful.

After discussion of the results it was decided to run two additional “optimization” experiments. First, the results from tests 4 and 7 seemed to be amongst the best, so the parameters for these two tests would be averaged. This generated test X1 as described in Table I. The results from this test produced the highest orthophospite efficiency but also produced the highest volume of waste per MTO. Also, during the run the orthophosphite in the bath could not be kept constant, rising from 145 to 190 g/L (Fig. 4).

The second test was modeled after test 7, which withstood a very punishing day. In this test the orthophospite in both the plating bath and the C2 tank were highest. We modified this test by allowing the orthophosphite in the C2 tank to go as high as it could go because the DOE calculations pointed in this direction and we knew that this would help reduce the volume of waste. This generated test X2 as listed in Table I. Table II shows that test X2 was the most successful test. The plating bath was maintained at steady state during the test (Fig. 4) and the volume of waste per MTO was less than that obtained during Bleed and Feed operation.

The most important result of the DOE is that even though the tests did not produce an optimum within the bounds of the original parameters, the results and the calculations from the DOE


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program showed the direction in which other experiments should be conducted. The optimum was outside the bounds of the original set of parameters as indicated by the calculations.

The data in Table II show that during test X2 the nickel and hypophosphite losses were 0.84% and 16.4% respectively. The orthophosphite efficiency was 117%, meaning that the ED unit took out a little more orthophosphite than the plating bath generated. During this run 150 L of waste was generated for each 3 g/L MTO or about 75 L for a traditional 6 g/L MTO and the plating tank was 2200L. In our previous discussion of ED strategies [8] we provided a table like Table III showing the wastes for three other strategies.

**Table III Comparison of ED Design – Waste Generation and Material Losses**

| Design | Waste Volume (vol%/6g/L MTO) | Nickel Losses (%) | Hypophosphite Losses (%) |
|---|---|---|---|
| **Batch (field)** | 12.7 | 28 | 85 |
| **Frequent Batch (lab)** | 18.7 | 3.5 | 10.7 |
| **Continuous High Temperature (lab)** | 16.8 | 2.2 | 8.3 |
| **Continuous Low Temperature (field)** | 3.4 | 0.84 | 16.4 |

The data in Table III for the Batch and the Continuous Low Temperature methods were obtained in plating shops under normal production conditions. The data from the other two methods were obtained in the pilot lab. This table shows that the Continuous Low Temperature method provides significant reduction of all parameters compared with the Batch method. There are plans to build and test a Continuous High Temperature unit under production conditions.

**Costs**

Costs are important to any industrial operation. There are costs for the plating bath and for the ED unit.

During the operation of the plating bath there are two additives that are normally added at a 1:1 ratio, the nickel containing S and the hypophosphite containing R. The data shows that very little nickel metal ions are lost through the ED membranes so the amount of the S component used during ED would be similar to that used during normal operation. However, the R component for ED must be reformulated especially for ED. The R-ED component contains extra materials, including sodium hypophosphite, such that it is about 30% more expensive to make than normal R. Thus, the reformulated R-ED would be added with the S component at about a 1:1 ratio, but would add extra hypophosphite. That extra hypophosphite is removed from the plating bath with the orthophosphite. Table IV shows that about 60.4 Kg of this extra sodium hypophosphite is transferred to the waste tote during 10 MTO of operation and this represents a loss of about 16.4% of the total sodium hypophosphite (Table III).


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The maximum electrical consumption of the ED for EN unit is about 8.5 kW. This assumes that the chiller (a large electrical consumer) is operating full time. During this run some of the cooling was obtained with a coil immersed in a rinse tank.

Waste volume is an important cost. The plating tank volume is 2200 L. During the Bleed and Feed operation 1/6$^{th}$ of the plating bath volume is removed from the bath every time that two 3 g/L MTO have been added to the bath. Thus abut 1833 L of plating bath becomes waste during 10 MTO. During the X2 test 1510 L of waste solution was generated. Table IV shows the losses of materials for the two methods

**Table IV Waste Generation of Bleed and Feed vs. Continuous Low Temp. ED**

| | Bleed & Feed | Continuous Low Temp ED |
|---|---|---|
| **Waste Volume 10 MTO** | 1833 L | 1510 L |
| **Ni Concentration (g/L)** | 3.0 | 0.4 |
| **Hypo Concentration (g/L)** | 20 | 40 |
| **Total Ni Wasted (g)** | 5500 | 483 |
| **Total Hypo Wasted (Kg)** | 36.6 | 60.4 |

The Bleed and Feed method wastes more than 10 times the quantity of nickel metal ions. On the other hand the Low Temp. ED method wastes about 1.7 times more hypophosphite than the Bleed and Feed method.

During the planning of this trial the use of a Reverse Osmosis (RO) unit was considered to obtain a reduction of the volume of wastes. However, it was determined that the high salt content of electroless nickel wastes makes RO impractical.

In summary, the costs and wastes for the two methods can be compared:

1. The Bleed and Feed method produces about 21 % more waste volume.
2. The Bleed and Feed method wastes about 11.3 times (not 11.3%) more nickel metal than the ED method.
3. The ED method wastes about 1.7 times more hypophosphite than the Bleed and Feed method.
4. The ED method uses a special hypophosphite containing “R-ED” component that is specially formulated for ED and costs about 30% more to manufacture than the R component used for normal and Bleed and Feed operations..
5. The ED method does NOT need 1/6$^{th}$ (16.7%)of the bath to be made up fresh every 2 MTO.
6. The ED unit uses a maximum of 8.5 kW.
7. The ED unit costs about US$50,000-100,000 depending on size and configuration. However, a lease agreement can help manage this cost.

While this list does not provide a specific dollar (or Euro) quantity, any shop operator can determine the cost differences from local chemical and energy prices.


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## Conclusions

The Continuous Low Temperature ED unit is a viable waste reduction alternative for electroless nickel plating processes. This paper has presented the design of the unit and provided a discussion of DOE experiments that helped to find the optimum operating conditions for the unit at a particular production shop. The DOE experiments were set up with what seemed to be reasonable parameters. However, the optimum was outside the bounds of the DOE experiment set. The DOE calculations did, however, provide important data pointing the direction in which further experiments should be conducted. This provided important guidance that helped find an optimum for a complex process with just 10 experiments.

The Continuous Low Temperature ED unit compared to normal operation and bleed and feed operation:

1. Produces about 21% less waste volume than traditional EN operation methods and Bleed and Feed operation.
2. Wastes about 11.3 times less nickel metal ions
3. Does not require makeup chemistry at the end of bath life for traditional EN operation.
4. Does not require incremental makeup chemistry as required for Bleed and Feed operation.
5. Uses a hypophosphite containing “R-ED” component that costs 30% more to manufacture.
6. Has larger hypophosphite losses than traditional or Bleed and Feed operation.

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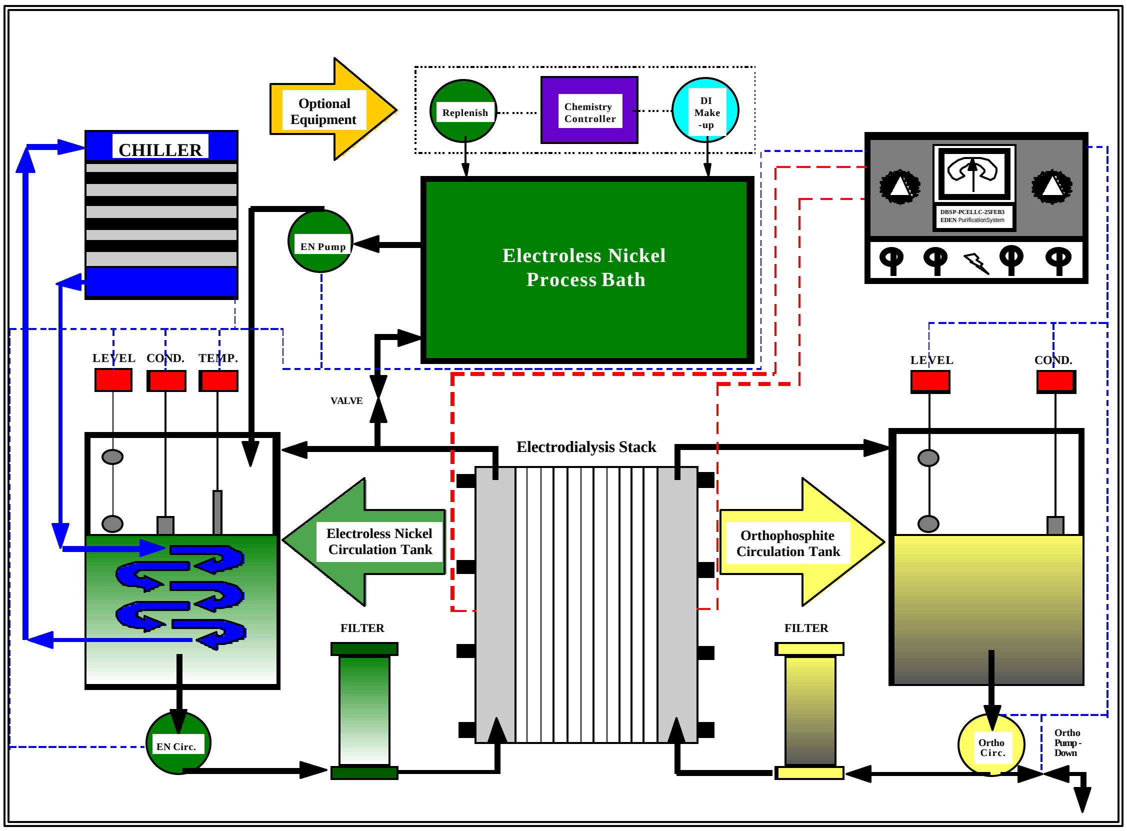


Tank C1 Tank C2

*Fig. 1. Schematic of the Continuous Low Temperature ED system.*

**524**


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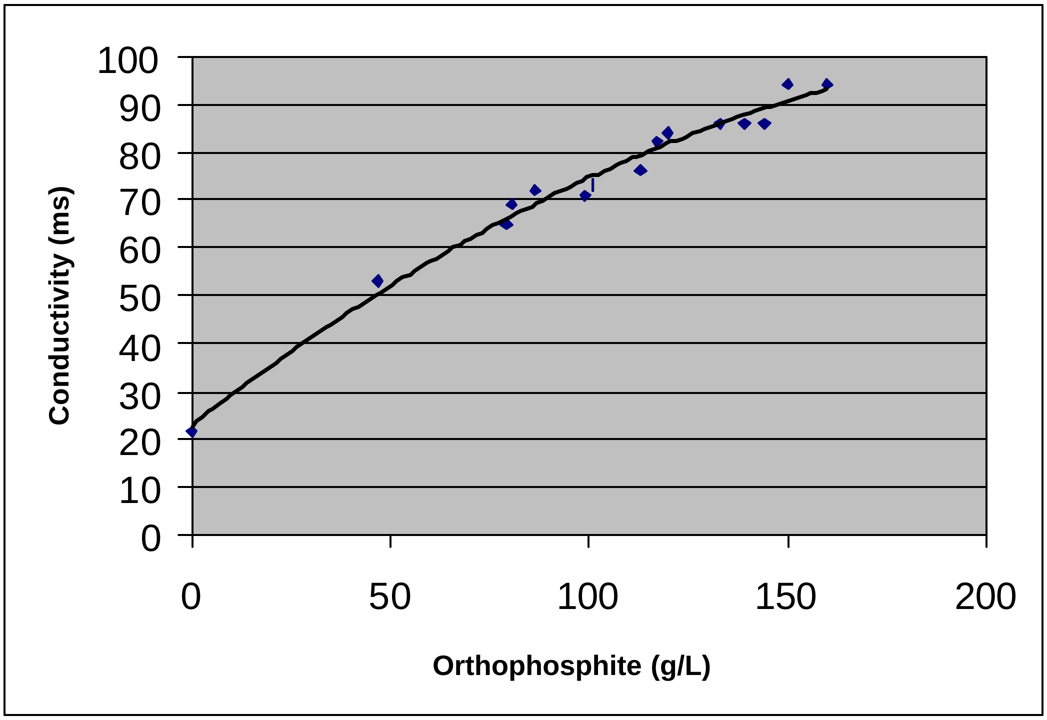


*Fig. 2. Conductivity of electroless nickel process with increasing sodium orthophosphite concentration.*

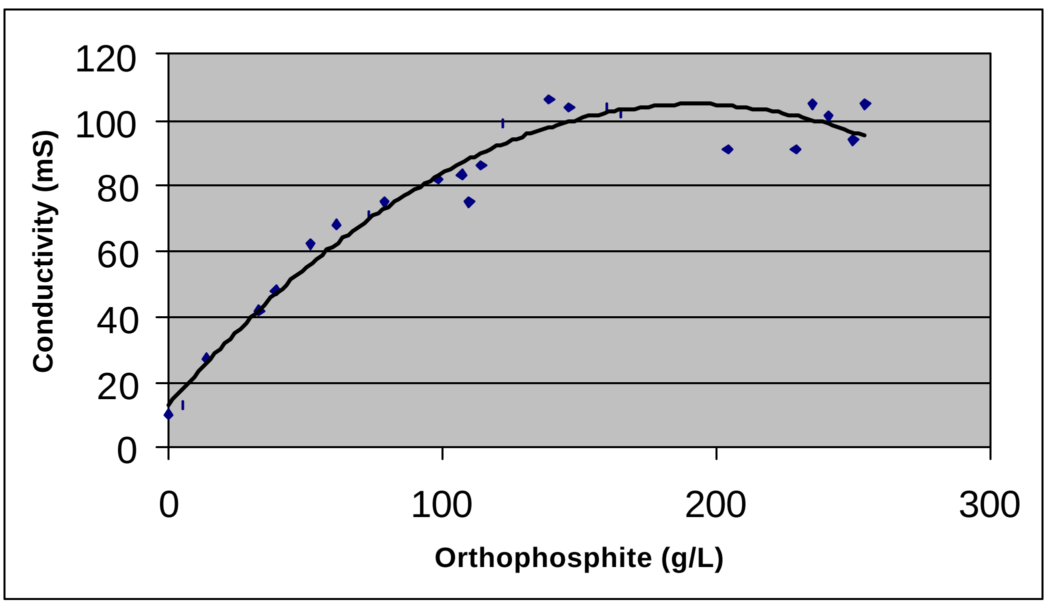


*Fig. 3. Conductivity of waste salt solution (Tank C2) with increasing sodium orthophosphite concentration.*


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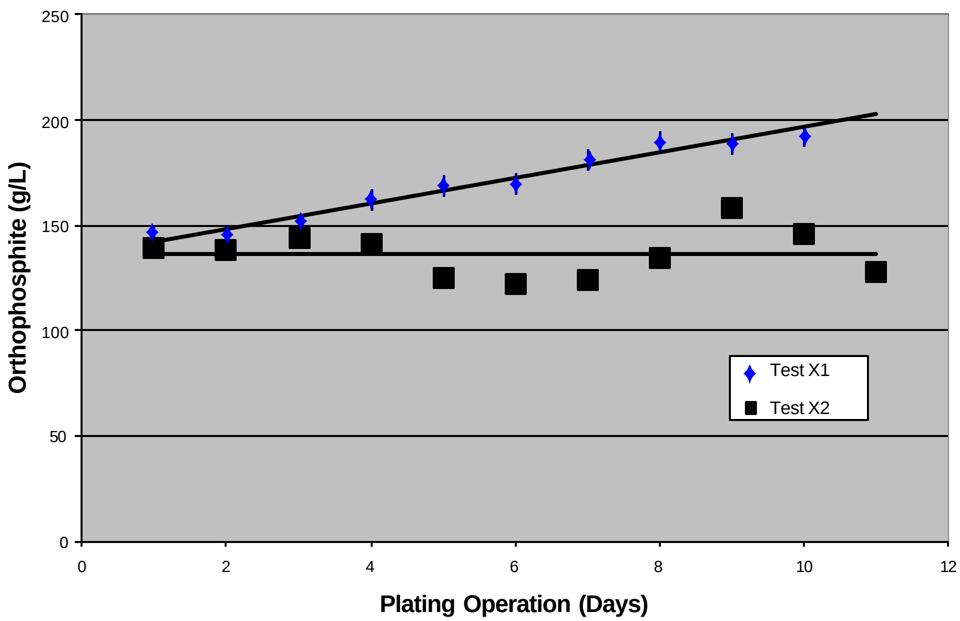


*Fig.3. Sodium Orthophosphite concentration for tests during electrodialysis maintenance tests X1 and X2 over time.*


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