Insoluble anode technology for electro-tinning lines

The application of Techint insoluble anode technology in new and existing tinning lines minimises the amount of sludge, and hence loss of tin. Other benefits are reduction of manpower for anode handling, improved coating quality, better process control, and elimination of phenol vapours inside the building.

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Because of the necessity to improve strip quality, reduce labour, pollution, and tin over-coating in electro-tinning lines using soluble anodes, Techint Technologies, a division of the Techint Group, and Centro Sviluppo Materiali (CSM), have researched potential improvements and developed a new tin dissolution process. This is able to minimise the amount of sludge and loss of Sn(IV) and has been successfully proven through extensive tests on Siderar's tinning line.

The Ferrostan process, based on the use of soluble tin anodes in Phenol Sulphonic Acid (PSA) solution, is well consolidated in electro-tinning lines. The use of soluble anodes is advantageous because the tin plated-out on the strip can be automatically produced by the dissolution of tin from the anodes. However, there are disadvantages.

The most important disadvantage is the necessity to drain off the plating solution because of the different electrochemical efficiency in plating and dissolution. An increase of tin concentration in the plating solution is unavoidable with the use of tin anodes, and dilution of the solution generates overflow and discharge, with loss of expensive material and possible water pollution, unless adequately treated.

The conventional equipment used worldwide for the removal of excess tin is the insoluble anode. Many customers today have one half cell equipped with insoluble anodes, but it is very difficult to control the solution and concerns about a rapid decrease of tin and an increase of free acid in the plating solution make the use of insoluble anodes in this way less practical. Other disadvantages of the Ferrostan process are the fumes exiting the plating tanks, labour requirements for handling the tin anodes and low productivity.

Additionally, market demand is towards tinplate with thinner coatings; indeed for some uses tin coatings down to 0.2–0.4g/m^2 are required, causing production problems. With conventional electroplating technology the homogeneity of tin coating thickness decreases as the coating weight decreases, due to the particular geometry of the tin anodes, which do not present a continuous surface. In fact, each anode is formed by a series of vertical bars drawn against each other so as to leave only a minimum space between the bars, which may produce a lower tin thickness. Another cause of irregular tin coating derives from non-uniform consumption of tin bars, which, in turn, gives rise to preferential current distribution. For thicker coatings such situations are alleviated, since more cells are employed in the sequence of electroplating steps, thus allowing the tin coating to grow more uniformly.

With soluble anodes the standard deviation (σ) of coating thickness increases as the coating thickness decreases, whereas with insoluble anodes it is independent. High σ values are not allowed, for instance, in tinplate for the fabrication of two-piece DWI cans where, owing to wall ironing, the tin coating is reduced and could disappear in those areas where the coating thickness is not homogeneous.

One solution to these problems is to equip an entire tinning line with insoluble anodes. The anode then has a continuous surface, and very thin tin coating layers can be produced with high thickness homogeneity. Nevertheless, the use of non-soluble anodes still requires a tin dissolution reactor, connected to the electro-tinning line to replenish the amount of tin deposited on the strip. Considerable research was done to dissolve (chemically or electrochemically) the tin in the plating solution, an industrial process was set up many years ago and a few plants, mainly in Japan, are working with insoluble anodes.

The process of chemical tin dissolution, using oxygen to accelerate the oxidation reaction of metallic tin to ionic tin, cannot avoid the formation of a Sn(IV)-based sludge and, as a consequence, loss of tin, sludge disposal and waste water treatments made this process inconvenient. Techint, in cooperation with CSM, decided in 1998 to develop an innovative process for dissolving the tin with minimum sludge formation.

The main advantages of tin plating with insoluble anodes are summarised in *Table 1*.

Chemical reactions

The main reactions involved in the metallic tin dissolution process are:

1. $2Sn + O_2 + 4H^+ \rightarrow 2Sn^{2+} + 2H_2O$
2. $Sn + O_2 + 4H^+ \rightarrow Sn^{4+} + 2H_2O$
3. $2Sn^{2+} + O_2 + 4H^+ \rightarrow 2Sn^{4+} + 2H_2O$
4. $Sn^{2+} + 2PSA \rightarrow Sn(PSA)_2$

(PSA: Phenol Sulphonic Acid)

5. $Sn + Sn^{4+} \rightarrow 2Sn^{2+}$

Oxygen is necessary to enhance the reaction rate of the oxidation of tin by the acidity of the bath formed at the insoluble anode. The electrochemical reactions occurring at the electroplating site with insoluble anodes are:

6. $2Sn^{2+} + 4e^- \rightarrow 2Sn$ (cathode)
7. $2H_2O \rightarrow O_2 + 4e^- + 4H^+$ (anode)

The acidity formed at the anode in the dissolution reactor restores the two moles of tin deposited on the strip. Thus the mass balance is assured.

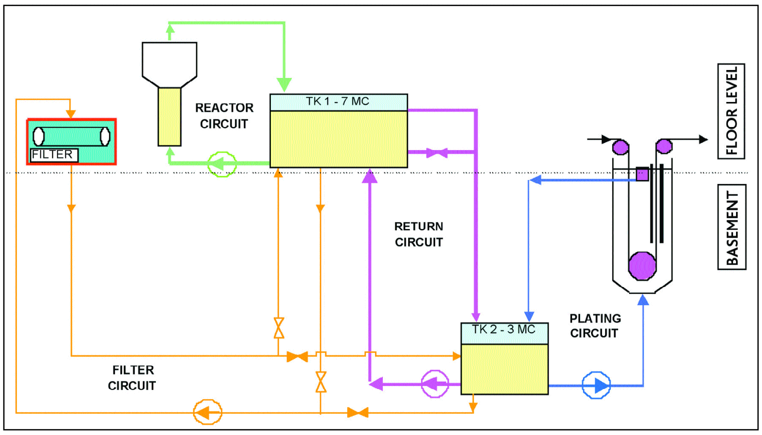
Pilot laboratory line

The process is based on the oxidation of metallic tin granules in the Ferrostan-type tinning electrolyte saturated with pure oxygen. A 30 litre pilot reactor for tin dissolution was initially produced at the CSM laboratories. (see *Figures 1* & 2). The plant comprises a tin dissolution section and a tin electroplating section. The dissolution section contains the chemical reactor, the pressurising pump, the oxygen feeder and the tank for the preparation and storage of the solution. The PSA electrolyte flows through the reactor by means of a pump operating at a pressure of up to 8 bar. Oxygen is fed into the impoverished electrolyte by a special feeder designed to minimise the size of oxygen bubbles and promote their immediate dissolution. The electroplating section has a vertical electrolytic cell with flat parallel electrodes, a pump for solution movement and a recirculation tank. Since the tin dissolution rate is proportional to oxygen activity, oxygen-saturated electrolyte at pressures higher than 1 bar, are used. A nozzle for feeding oxygen into the solution was developed for this purpose.

The dissolution of metallic tin achieved through oxidation in acidic environment by dissolved oxygen

Parameter	Benefit
Constant tin covering on strip	Less tin consumed
Better edges coatings	Better strip quality, particularly important for thin
No anode handling flexibility,	Reduced labour costs, higher productivity and safer and better working environment
No anode melting plant	Reduced labour
Covering on tanks	Less fumes
Electrolyte always under control	Lower electrolyte discharge, consumption and pollution
Anodes closer to strip	Reduced electricity consumption

● **Table 1** ***The main advantages of tin plating with insoluble anodes***



● **Figure 1** ***Schematic of the laboratory pilot plant for tin dissolution/plating***

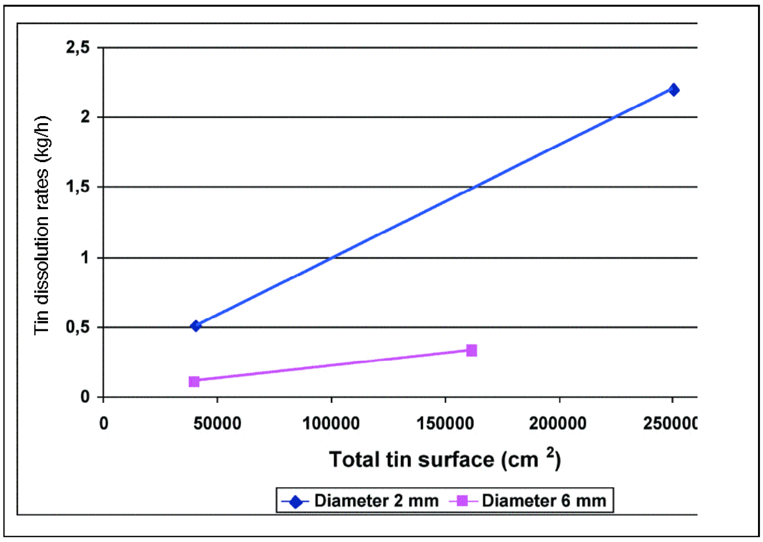
involves two main technological problems: First, to get the maximum solution of gaseous oxygen, possibly up to its saturation, even when working under pressure. Second, to maximise the mass transport coefficient using a fluidised bed reactor, which also minimises the non-reactive volume of the tin charge.

Tests were carried out by varying the following parameters:

- Oxygen flow rate
- Height of the fluidised tin bed
- Surface area of metallic tin
- Electrolytic solution flow rate
- Tin particle size

An additional test was performed at high temperature (~60°C) to evaluate the influence of this parameter on the dissolution kinetics and sludge formation.

● **Figure 2** ***Dissolution section of the laboratory pilot plant***



● **Figure 3** ***Effect of surface area and particle size on the amount of tin in the sludge***

The effect of the above parameters on the tin dissolution rate and the sludge production are now described.

Results of the laboratory dissolution tests

The results showed that tin lost in the sludge was lower than 8% of the total dissolved tin. Because Sn^{2+} production rate is proportional to the oxygen flow rate, by using a sufficiently stirred bed up to 95% of the feeding oxygen reacts effectively with metallic tin within the reactor. Conversely, the results show that the oxygen flow rate has no influence on the generation of sludge, since the percentage of tin lost in the sludge remains constant at varying oxygen flow rates. High temperature operation at about 60°C does not cause an increase in sludge formation, and increasing values of solution flow rate result in increased tin dissolution rates. At constant solution flow rate and tin granulometry, an increase of tin surface area (tin mass), leads to an increase of Sn^{2+} productivity.

It was also determined that a minimum superficial velocity (the linear speed expressed in m/s due to a given solution flow rate divided by the area of the reactor section) must be overcome to get an acceptable Sn^{2+} productivity. This can be explained because a significant surface speed makes the whole tin surface available for the oxidation reaction, reduces the diffusion boundary layer of O_2 and prevents the formation of preferential paths of the solution into the tin particles. Thus, to carry out a correct scaling up of the process it is necessary to take into account the stirring of the charge, which must be high enough to prevent preferential paths of the solution, but not too high to avoid excessive sludge formation.

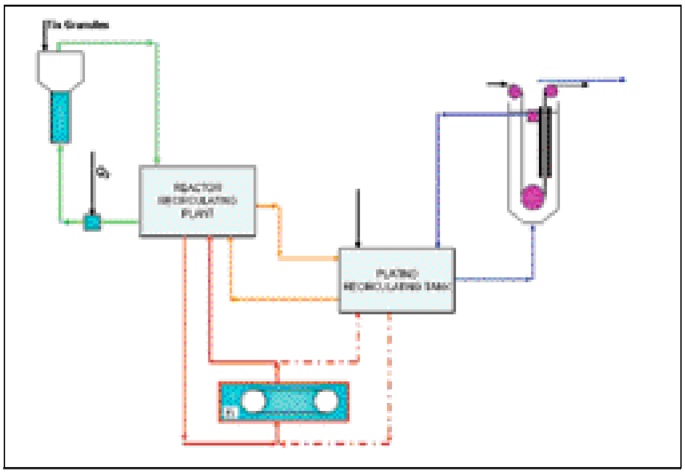
The surface area of the charge also plays an important role with two important effects linked to an increase of the specific surface area of metallic tin:

- Increased tin dissolution rate and Sn^{2+} productivity
- Decreased formation of sludge

The increase of surface area can be obtained using tin particles with smaller diameter, which require a lower solution flow rate. Moreover, small particles allow the design of a more compact reactor for the same productivity and require pumps with lower power, with possible advantages for energy savings. *Figure 3* shows that an increase in specific surface area of tin particles leads to increased dissolution rate. A drastic reduction of Sn loss in the sludge is observed when the surface area increases.

Pilot plant connected to an industrial line

In a further phase of the work an industrial-scale reactor equipped with insoluble anodes was produced to feed an electrolytic cell in the electro tinning line of Siderar Works in S. Nicolas, Argentina. Techint Technologies decided to design the pre-wetting tank so that it could be used either as a normal pre-wetting tank or as an insoluble anode plating tank connected to a dedicated tin dissolution plant for replenishing the plated-out tin.



● **Figure 4** ***Schematic of plant at Siderar Works***

● **Figure 5** ***Reactor vessel***

The tin dissolution plant was erected, connected to the revamped line and began operation at the beginning of 2001. By the end of the same year the research activity was completed. The schematic flow diagram of the plant is shown in *Figure 4*.

The plant consists of a reactor into which irregular sized tin pellets of about 2mm diameter, are charged into the metallic tin bed from the top of the reactor, four recirculating circuits and two recirculating tanks, one of which was already existing in the old line. The first circuit feeds the plating tank from which the low tin ion content solution is returned because of the deposition of tin on the running strip; and a second circuit connects the two recirculation tanks. A third, and most import circuit, feeds the tin dissolution reactor. This circuit works at high pressure (4–5 barg) in order to provide high solubility of oxygen in the solution. The fourth circuit removes the sludge from the solution. The tin dissolution plant has a design capacity of 30kg/h of dissolved tin. The charging system was designed with automatic valves to maintain the recirculation inside the reactor during the charging operation. The tin is charged in the reactor every two to three hours depending on the tin dissolution rate set in the plant, and the call for charging is performed by the plant automatic system when the quantity inside the reactor has reached a minimum value.

The reactor is a vertical cylindrical vessel, divided in two parts: the upper part (see *Figure 5*) has a large diameter to prevent the small tin particles escaping from the reactor. The total volume is about 1m^3.

The plating solution is fed from the bottom into the reactor through a distributor that supports the metallic tin particles and distributes the solution. Before entering the reactor, the solution is enriched in dissolved oxygen.

Suitable heat exchangers are installed in the circuits in order to maintain the plating solution at a constant temperature and, because of the drag-out from the plating tanks in order to keep the level constant in the two recirculating tanks, a refilling of solution from the normal line is available. The plating tank is equipped with insoluble anodes located in the tank as shown in *Figure 6*. The Iridium covered titanium anodes are connected to two rectifiers each having a capacity of 4,000VA. The replenishing rate of the plant is controlled by the flow rate of the oxygen. *Figure 7* is a schematic of the replenishment plant.

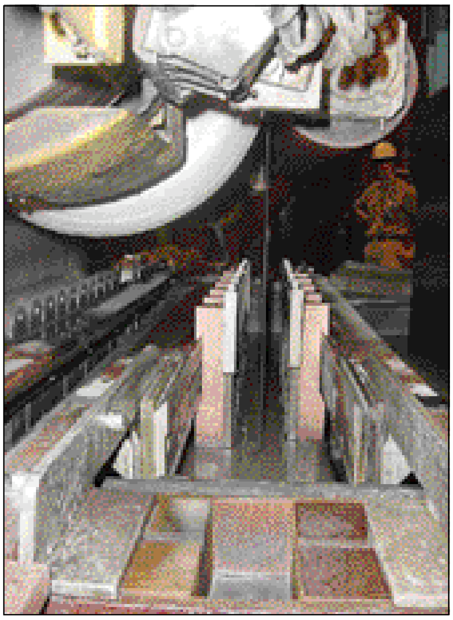
The plant can work in three modes:

- At constant oxygen flow rate (manual)
- At constant tin dissolution rate (auto 1 mode)
- At a rate proportional to the current given by the rectifiers (auto 2 mode)

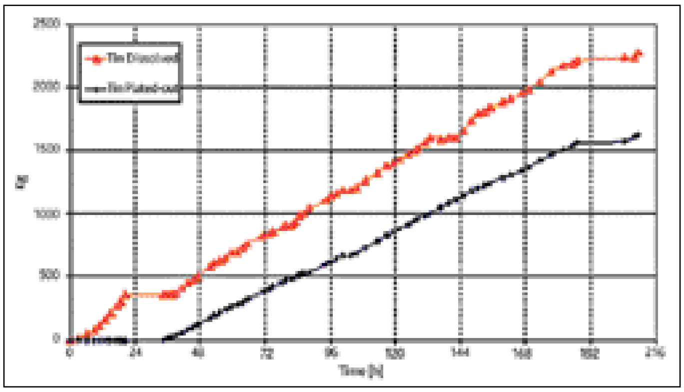
This last mode permits working at constant tin concentration in the solution because the replenishing rate is calculated taking into consideration the tin plated out at any given moment. A simulation model was developed to provide a continuous on-line calculated value of actual dissolution rate, based on the following main process parameters: tin charge, pressure, temperature, injected oxygen and recirculating solution flow rate.

Results of tin dissolution plant tests

After the start-up of the plant, a continuous campaign with simultaneous dissolution and tin-plating was performed from June to December 2001. No problems were encountered with the line operation or product quality and during the test operation the plant worked mainly at constant tin dissolution rate for calibration purposes. A typical behavior of both tin dissolved and tin plated along a continuous test is shown in *Figure 8*. In the first 24



● **Figure 6** ***Insoluble anodes in-situ***

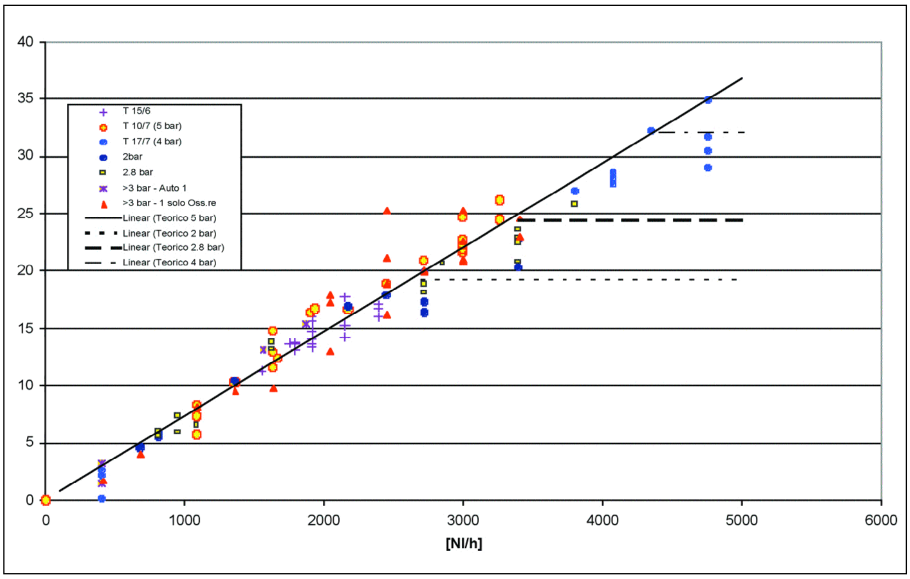


● **Figure 7** ***Flow diagram of replenishment plant***

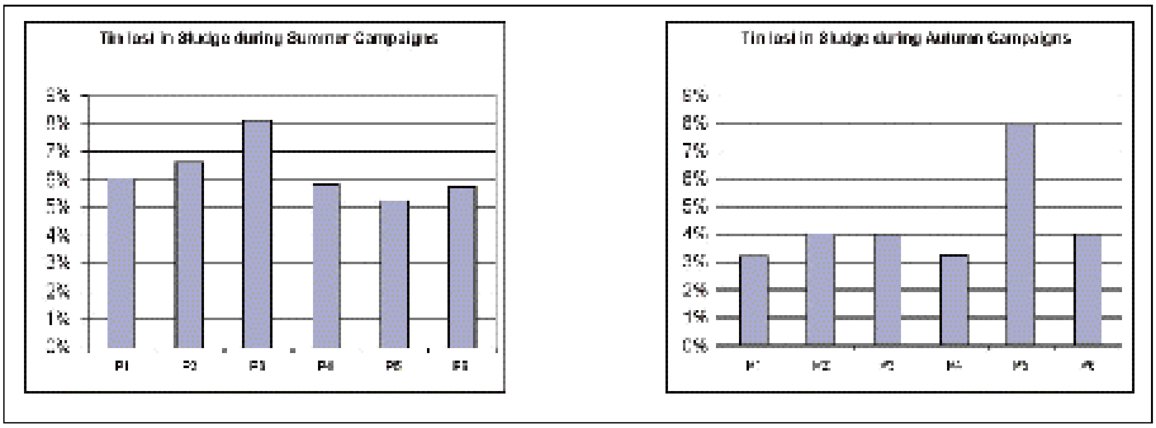
hours the plant works in dissolution mode only, in order to prepare the plating solution starting from virgin electrolyte (consisting of demineralised water and PSA). Once the desired Sn^{2+} concentration of about 35g/l is reached, the injection of oxygen is stopped, the brightening additive is added and for about 12 hours the plant works in recirculation mode only to mix the plating solution to avoid foaming and quality problems on the strip. After that preparation period, and good results from the Hull cell tests, the simultaneous dissolution and plating can start.

It can be seen that the dissolved tin is higher than the plated-out one. This is because of the drag out with the strip. Since the insoluble anodes are mounted on the first plating tank there is drag in of water and drag out of solution. The consequence is a dilution of the electrolyte with the necessity of dissolving more tin to maintain the Sn^{2+} concentration. The behavior of the plant was tested in different operating conditions by varying one parameter and keeping the others constant. The dissolution rate was found always to depend on the oxygen flow rate while working in conditions of full solubility of oxygen according to Henry's law. This was demonstrated at reactor pressures of 2, 3 and 4 bar.

The capacity of the dissolution plant versus the oxygen flow rate was tested in the summer trials, where the maximum dissolution rate was about 32kg/h. At each test, the quantity of generated sludge was weighed and correlated with the dissolved tin. Depending on the operating conditions (pressure, injection of oxygen, tin charge, solution flow rates, and so on), different quantities of tin lost in the sludge were measured, ranging from 5–8%. (see *Figure 9*). The tin dissolution rate could easily be controlled in the range of 5–35kg/h by adjusting the oxygen flow. The sludge can be generated both in the dissolution and



● **Figure 8** ***Dissolved and plated-out tin results***



● **Figure 9** ***Tin lost in sludge: comparison of summer and autumn campaigns***

plating circuits. The weighed amount is the total from the two circuits.

The tests were stopped for the summer holidays and when they started again in autumn the plant was set up in the best operating condition determined from the results of the summer tests. The results were very good (see *Figure 10*); the plant was able to reach a dissolution rate higher than 40kg/h without loss in efficiency and without higher generation of sludge. The sludge percentage was lower than in the summer session, with a maximum rate of 4%; the only exception being in the fifth campaign when the plant was set outside the standard conditions for a final check.

Results of plating tests

No detailed investigations were possible on the tin-plated strip produced, however, only with the insoluble anodes and the relevant rectifiers, was it possible to produce 1.4g/m^2 tinplate at an acceptable line speed of 100m/min. Samples were produced using only cell 1 and were checked by SEM/EDS analyses in comparison with tinplate produced with the current soluble anodes process. No difference in crystal shape or degree of coverage was detected.

Conclusions

Techint Technologies, in cooperation with CSM, have successfully developed a new technology for tin plating with insoluble anodes. This considerably reduces the quantity of generated sludge and consequently the loss of tin. This technology was proven on a pilot plant connected to an industrial line confirming the possibility of having a total yield of tin in a tinning line with insoluble anodes equivalent to a traditional line with soluble anodes.

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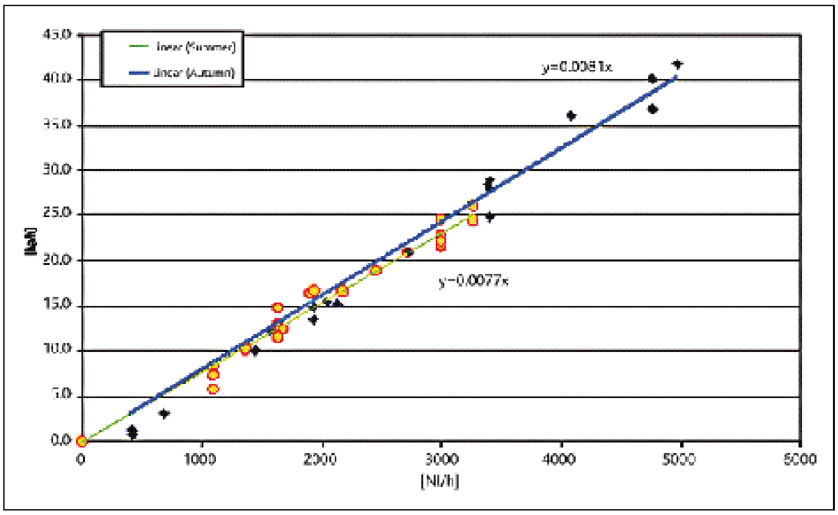

● **Figure 10** ***Reactor productivity, comparison of summer and autumn campaigns***