REPORT

on a visit to three advanced western chlor-alkali production plants employing the mercury technology, made by a group of Russian specialists from February 12 to 19, 2006

1. SUMMARY

1.1. Objectives

Russian experts in chlorine production went on the aforesaid visit mostly with the main objective to see and learn the ways by which the technical problems connected to the controlling of the emission of mercury into the environment were being solved at modern western chlor-alkali plants using the mercury technology.

1.2. Results

A group of Russian specialists composed of Executive Director of Association "RusChlor" Mr. Boris Yagud, Chief Engineer of Volgograd Public Joint-Stock Company "Kaustik" Mr. Sergeij Sergeev, Sales Director of Volgograd Public Joint-Stock Company "Kaustik" Mr. Yurij Kalmykov, Chief Researchers of Association "RusChlor" Mr. Valentine Eberil' and Mr. Peter Mironov, and the head of Technology Department of Volgograd Public Joint-Stock Company "Kaustik" Mr. Roman Aijrapetyan visited from February 12 to 19, 2006 the chlor-alkali plants of West-European companies "AKZO Nobel", "SolVin", and "Syndial" in correspondingly Germany, Spain, and Italy.

Managers and engineers of the said plants visually demonstrated to the Russians all the electrolysis production lines functioning with the mercury technology, answered all the asked questions, and provided the visitors with all the relevant information on the matters of their interest. Among all the raised issues the ones related to the engineering solutions used in controlling the emission of mercury into the air, water, products, and soil were of a special interest. Some of the answers were given not only in the form of

demonstrations or oral explanations but also given as technical drawings and/or texts in electronic form. At two of the three inspected plants the Russians were allowed to take photographs of whatever equipment they liked.

1.3. Preparation, organization, and financing of the visit

The success of the visit owes greatly to the efforts of Mr. Dyer and Ms. Barnes of Arctic Countries Actions Plan and US EPA, Mr. Yagud and Ms. Andreeva of association RusChlor, Mr. Debell of association EuroChlor, Mr. Caicedo, Ms. Tuxen, and Ms. Villalpando of UNEP. The visit would have been impossible to conduct without UNEP's financial support.

2. *A BRIEF CHARACTERISTIC OF THE INSPECTED PLANTS*

Each plant's annual output of chlorine exceeds 10^5 tons. At each plant the electrolysis is being performed within electrolyzers equipped with the amalgam decomposers of a vertical type and the metal-oxide anodes being continuously controlled forvoltage by an automatic control system.

At each plant the magnitude of the electrical current through a single electrolyzer exceeds 100 kA while the density of that current ranges from 12 to $14\frac{kA}{m^2}$. The temperature of brine as measured at the input of an average electrolyzer ranges within the interval from 70 to 75 degrees centigrade while the temperature of brine as measured at the output of the electrolyzer ranges within the interval from 80 to 89 degrees centigrade. The value of the pH factor of the brine being fed into the electrolyzers at each of the plants ranges within 3 to 4 units, while the hydrogen content of the chlorine ranges within 0.2 to 1.0 per cent.

For a packing substance for the amalgam decomposers is being used either pure graphite as is exactly the case at the AKZO-Nobel and SolVin plants or graphite preliminarily activated under a DeNora method as is the case at the Syndial plant. If in the later case the chemical activity of the packing substance lessens, small amounts of a molybdenum salt is added into the decomposers.

At all the inspected plants various metal-oxide anodes of "Runner" type are used. The coating of such an anode is supposed to be based on iridium, ruthenium, and titanium oxides. The anodes are supplied by either company "DeNora" as is the case at the plants of companies "AKZO-Nobel" and "Syndial" or company "Solvay" as is the case at the plant of company "SolVin". Each plant's managers consider the anode's running time before maintenance a random variable varying within the interval from 4 to 8 years depending on the density of the electrical current, temperature at which the electrolysis is going on, and some other parameters. Nevertheless, on the average the anode's life would be the longest at the "AKZO-Nobel" plant ceteris paribus.

There have been noticed differences there in the inspected plants' practices of regulating the voltage and protecting the anodes against the short-circuiting. At the "AKZO-Nobel" and "Syndial" plants the said systems regulate anodesgrouped into 4 to 6 sets. Each group is mounted onto its own frame equipped with its own actuating mechanism so that the anodes of that group could move up and down. In so doing, the obligatory air-tightness is maintained by either a number of Teflon bellows each being arranged in such a way as to seal the spot of inputting a conductor rod through the lid as is exactly the case at the "AKZO-Nobel" plant or a soft Teflon carpet sealing the whole group of anodes as is the case at the "Syndial" plant. In contrast to this anodes are being regulated individually at the "SolVin" plant. In so doing, each anode is equipped with its own electric motor with a separate actuating mechanism. The obligatory level of air-tightness is being maintained there with the use of special toroidal stuffing-boxes.

At all the three inspected plants the uniformity of distribution of the electrical current over the anodes is being continuously monitored so that if such an anode is spotted up that is persistently demonstrating an excess of the electrical current through it, a decision could be immediately taken there to regulate that anode individually. At all the three plants the voltage applied to an electrolyzer is ranging within from 3.9 to 4.2 V.

At all the three inspected plants both the input and output boxes are air-tightly closed. The floorings of all the electrolyzer halls are made of sequential layers of plastic, concrete, epoxide resin coating and equipped with a complex system of drain pans, clean-out pits, traps, and vacuum-collectors designed in such a way as to trap, collect, and return the spilled mercury back to the productive cycle as soon as possible. The lighting of both the electrolyzer hall and the rest of the working zone is given much attention at each plant.

There is implemented a system at each plant of continuous monitoring of mercury content of the electrolyzer hall air with the use of both mobile and stationary meters.

There is imposed a rule at each of the three inspected plants according to which if an electrolyzer is switched off for maintenance, it should be immediately covered with a special lid so as to prevent the mercury that is contained within the electrolyzer from escaping it. Another rule that is also in force at some plants stipulates that the temperature of any electrolyzer that has been switched off for maintenance should be kept at a level not lower than 60 degrees centigrade in order to preserve mercury tightness of the seals of that electrolyzer. Managers of each inspected plant are used to scheduling the maintenance works in such a way as to do simultaneously on each electrolyzer switched off for maintenance as many different works as possible (grouping the interventions).

Except in the SolVin plant, where there is also a forced ventilation on each cell, all the plants use natural ventilation of the cell room. On the grounds that the overall level of the emission of mercury from both the electrolyzers and amalgam decomposers into the environment has been made rather low at each inspected plant, managers there have rightfully not installed forced ventilation of the electrolyzer hall. The mercury content of the air of each plant's working zone does not deviate considerably from the level of 5 to 10 µg/m^3 which is now being widely considered a good achievement.

At all the three inspected plants the state of the personnel's health is being periodically controlled so that every employee's urine is checked for its mercury content at least once in every three months (for cell room workers).

Chemically pure salt is used as raw material at both "AKZO-Nobel" and "Syndial" plants. Nevertheless, the brine (part of the total flow) is being additionally purified there for calcium and magnesium as well. In order to facilitate the purification of the brine and make it more efficient there is used a so called "separate" model at the "AKZO Nobel" plant, which in essence means that 70% of the brine being treated is actually purified there of only iron under the pH factor being equal to 9 units while the remainder 30% of the brine being treated is purified of only calcium and magnesium under the pH factor being equal to 12 units. There is also built a sand filtering process into this scheme. Contrary to the practice of "AKZO-Nobel" and "Syndial", impure salt is being used at the "SolVin" plant. This implies a full cycle of soda-alkali purification of the brine, which in its turn involves a continuous precipitation process with the use of a Dorr precipitation tank. After the precipitation tank the brine finally goes through sand filters, and the slimes generated by these filters are then treated with sodium hydrosulfide so as to convert as much of the mercury contained in that slimes as possible from its toxic ionic form into an inert sulphide one. In the end the washed slimes (still containing some mercury sulphide) are firstly filtered with the use of a special press-filter and secondly buried on a special site.

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There is being continuously formed an excess of brine within the anolyte cycle of the general production process at the "SolVin" and "Syndial" plants. The mercury content of that brine amounts to $8 mg/l$. The said excess of brine is continuously being drained from the anolyte cycle so as to treat it with either sodium hydrosulphide under pH factor being less than 3 units as is exactly the case at the "SolVin" plant or thiourea as is the case at the "Syndial" plant. The slimes being worked out in the course of such a treatment contain mainly mercury sulphide. For that reason that slimes are periodically being dissolved in hydrochloric acid and sodium hypochlorite to convert the mercury into a soluble ionic form under the following reaction:

$HgS \downarrow + 4ClO^- \rightarrow Hg^{2+} + 4Cl^- + SO_4^{2-}$, which usually takes as long as 12 hours to come to an end at the outdoor temperature. The mercury having been dissolved in the course of that treatment is sent back to the anolyte cycle.

It is mostly the high quality of the brine used at each of the inspected plants that makes it possible to use electrolyzers there for rather a long period of time without any necessity of opening them for the cleaning of the bottoms, in-boxes, or end-boxes. Nevertheless, seemingly owing to that that at the "Syndial" plant the magnetizing force applied within the zone of electrolysis is highest (namely the unit capacity amounts to 460 kA and the density of the electrical current is as high as $14 kA/m^2$) as compared to that of the other two plants considered, the process of forming both the slimes and heavy amalgam oil on the bottoms of electrolyzers is going on there quicker. It is not surprising, then, that it is the "Syndial" plant where the engineers have introduced a clever gadget into the standard design of their electrolyzers. This gadget allows cleaning the electrolyzers' bottoms without opening the electrolyzers themselves. The idea is simple. The gadget is in essence a scraper mounted within the electrolyzer across its bottom in such a way as to allow the scraper to move over the whole surface of the electrolyzer's bottom pushed along by two parallel rods. The scraper being pressed to the inner surface of the electrolyzer's bottom by electro-magnetic force gathers the slime and amalgam oil worked out on that surface and pushes the gathered substance into the end-box. At the "Syndial" plant they perform such a cleaning procedure on each electrolyzer at least once in approximately every 20 working days.

There have been identified two quite distinctive ways at the three inspected plants by which the waste waters are being purified there.
At the "AKZO-Nobel" plant they purify the waste-waters by the following consecutive steps:

- precipitation;
- filtration;
- chlorination;
- disintegration of the remaining active chlorine;
- recovery of mercury with the use of ion-exchange resin.

The resultant mercury content of the purified waste-waters falls somewhere close to $10^{-6}\, g/l$.
At the "SolVin" and "Syndial" plants they are purifying the waste-waters under a sulphide method, which gives the mercury content of the water being dumped into the sea of approximately $5 \div 8 \times 10^{-6}\, g/l$.

At all the three inspected plants the hydrogen and off-gases are being purified under well-known and widely established procedures. The final purification is being conducted through sorption by either the activated carbon or the activated carbon impregnated with sulfur. It is worth noticing though that in so doing the off-gases are being gathered not only from the in-boxes and end-boxes but also from the air contained by every such piece of equipment where the mercury vapors can appear even if theoretically. Thus, they are gathering the off-gases from, for instance, brine tanks, anolyte filters, and some other pieces of equipment.

There is being applied the one and the same method of purifying the liquid caustic soda at each of the three inspected plants, which in principle is firstly to trap the droplets of mercury by a U-form trap and secondly to filter the caustic soda with a "Funda" filter. Owing mostly to the "Funda" filter performance, this simple approach yields rather good a result as the mercury content of the fifty-percent water solution of caustic soda is as low after such a treatment as 10 to 50 µg /kg NaOH 50 %.

At all the three inspected plants the regeneration of mercury from the solid wastes and dry slimes is being performed under a thermal procedure while the mercury residues are removed in washing the equipment before maintenance with either water or sodium hypochlorite.

The removal of rubber from the rubberized pieces of equipment for repair is being performed with the use of either the method of rapid cooling by liquid nitrogen within a special chamber as is the case at the "SolVin" plant, or the method of cutting the rubber off by a stream of water under a very high pressure (up to 2200 atm) as is the case at the "Syndial" plant.

There is being performed quantitative registration of the emission of mercury introduced into the environment by the same principles at all the three inspected plants:

- the emission with air is calculated as a product of the following two numbers: the average mercury content of the air within the working area, and the value calculated on the basis of a mathematical model of the flow of the air through that working area;
- the values of emission with water, solid wastes, hydrogen, and caustic soda are calculated each as a product of the following two numbers: the average mercury content of the substance being considered and the value of the output flow of that substance.

It is important to notice in this connection that in calculating the specific values of the above components of the emission of mercury into the environment they use the nominal value of the corresponding chlorine productive capacity rather than the production.

The values of the components of the overall yearly specific emission of mercury made by each of the three inspected plants in 2005 are shown in the table below in comparison with the analogue data of Volgograd Public Joint-Stock Company "Kaustik".

Types of the emission of mercury	**Amounts as measured in grams of mercury per a ton of the output Clorine**			
	AKZO-Nobel	SolVin	Syndial	JSC "Kaustik"
Air within the electrolyzer hall	0.639	0.666	0.600	1.129
Off-gases	included here above	0.197	-------	0.009
Products	0.048	0.063	0.050	0.615
Waste-waters	0.001	0.007	0.020	0.074
Solid wastes	0.019	Not communicated	Not communicated	9.560
Total	**0.688**	**1.000**	**0.720**	**11.387**

3. Some of the particular technical solutions implemented at the inspected "Euro Chlor" plants that have impressed the Russian visitors most

Russian experts have spotted out a lot of technological peculiarities in the production process of the inspected plants. Here is the list of those that have turned out to be both most impressive and directly related to the problem of reduction of the emission of mercury into the environment:

- system of automatic control of the voltage applied to the electrolyzers, which is capable among other things of protecting them against short-circuiting;
- anodes "Runner";
- sealing-in of both the in-boxes and end-boxes;
- temporary covers used in sealing-in the electrolyzers that have been switched off for maintenance;
- complex of the organizational and technological decisions aimed at preventing any violation of the air-tightness of the switched off electrolyzers;
- additional activation of the packing of the amalgam decomposers by the molybdenum salts;
- method of purification of both the waste-waters and anolyte wastes which in particular includes the following stages:
  - precipitation of mercury with the use of sodium hydrosulfide;

- leaching of mercury from the sulphide slimes with the use of both hydrochloric acid and sodium hypochlorite with the aim to return the recovered mercury back to the anolyte cycle;
- finishing purification of the waste-waters with the use of the ion-exchange resins;

- filtration of solution of the caustic soda with the use of filter "Funda";
- system of rapid gathering and returning of the spilled mercury back to the production cycle;
- processing by the sodium hydrosulphide of the slimes having come from purification of brine with the aim to convert the mercury being contained in these slimes into a sulphide form before dumping them for storage;
- purification off the mercury vapours of the air having come from the brine tanks and/or filters used in filtering the anolyte;
- methods of removal of the rubber from the rubberized surfaces;
- stationary, mobile, and in-line meters of mercury;
- system of monitoring the mercury vapour's content of the air of the working zone;
- system of monitoring the state of the health of the personnel in the aspects of mercury poisoning.

4. A general preliminary conclusion

The exchange visit being considered has turned out fruitful for the Russian visitors. During the visit there have been gathered vast domain of promising data related to practical aspects of counteracting the mercury emission at the inspected plants. That data is necessary to think over so that it could be possible to apply the lessons drawn from the Western experience to the practice of solving the problems faced by the Russian chlor-alkali producers of the Association "Ruschlor under the current Russian circumstances. This task should be tackled by the team of RusChlor's experts and practitioners in the field being considered in close cooperation with colleagues from Euro Chlor, UNEP, EPA, ACAP, and WCC.