Minimum Environmental Impact Via Riocell's Advanced Tertiary Level Wastewater Treatment

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ABSTRACT

Early 1980's Riocell decided to invest in an unique wastewater treatment facility to fulfill local authorities' restrictions. The bleached kraft pulp and paper mill has till now one of the most advanced effluent treatments in the world, comprising the following sequence of events: screening, neutralization, sedimentation, cooling, aeration, biological secondary treatment, flocculation with alum, sedimentation, polishing, neutralization and pumping to the river. As a result, final effluent shows very low pollution load in kg/admt of pollutants: AOX (0.15); color (27.7); COD (4.89); BOD5 (0.35); suspended solids (0.69). An overall description of costs, efficiencies, performances, strategies and eco-toxicological evaluations is presented.

To be minimum environmental impact: this is a today key wish of the pulp and paper industry. However, to be minimum impact does not mean to have only no odor in the gases or no color or AOX in the effluents. Also, environment must be considered as a whole, including forests, animals, people, community and pollutant discharges. You may become minimum environmental impact via new technologies to prevent pollution or adopting end-of-pipe measures to control pollution. I personally think that most of the pulp industry pollution problems will be solved in no more than one or two decades, by using lignolitic microorganisms (or enzymes) for cooking, bleaching and to control wastes. However, this is still to come. Today realities are kraft cooking, bleaching with chlorinated compounds and lots of wastes to be treated. Although costly, by treating gases, liquids and solid residues you may be,come very close to the zero impact. It is each one choice: shall I change technology or treat wastes?

Let's talk in this paper about ways to reduce pollution load in the liquid stream. My purpose is to bring to the table some information about Riocell's wastewater treatment plant and the approach the company is giving to the near future.

Riocell is a pulp and paper company located in the state of Rio Grande do Sul, in the Southern part of Brazil. The strategic drive of the company is to act in several niches such as eucalyptus market paper and dissolving grade pulps; unbleached pulps and printing and writing papers. Yearly the production is in the range of 280,000 to 310,000 admt, depending on the ratio among products. Main product is eucalyptus bleached kraft paper grade market pulp. Another hardwood, named black wattle or acacia, is used mainly for dissolving pulp runs.

The mill is located near Porto Alegre, a city of 1.5 million inhabitants in the right bank of the Guaiba river, a kind of ecological heritage to the local people.

The mill had problems with environmental authorities and the population when started-up in the 1970's. The company image was seriously affected at that time. Thus, special care and major capital investments were allocated in environmental control and pollution prevention. Environmental concern became a cultural strong point from the operators to the shareholders.

The environmental concept is to keep final residues at a minimum, recovering pollution" losses in the areas they are generated or transforming pollution in valuable sources of raw materials to other process or products. This philosophy, for example, has converted land-filling in an out-of-date technology in Riocell. In our case, 99.7% of all solid residues originated in the mill are transformed in saleable products with solid and safe market in the region.

The "Multi-Mills" Concept

As it was mentioned before, the concept is to avoid losses in the area where pollution is generated. This is perfect because people are educated to take care of their own garbage. The mill was divided in several small units such as pulp mill, paper mill, recovery boiler, evaporation plant, causticising, chemical plant, etc. Each one has own environmental internal standards to fulfill and to be monitored and controlled. They have to keep their effluents within very restrictive limits. They are not allowed to discharge effluents above the limits to the wastewater treatment plant. In case such effluents are generated, they must be brought back to the system and recovered by the area is generating it. To give feasibility to this policy, the critical areas have been isolated, tanks were erected to hold contaminated effluents and pumping stations were installed to keep losses at the area. The idea behind this was that the cheapest treatment is the one where losses are avoided. Each area has own responsibility and it is monitored as if it was an individual mill. The operators have soon learnt that it is very complicated to handle pollution back to their own heads, and creativeness came with amazing solutions. Today, many of these areas have closed completely the water cycle and have no more effluents.

Brief Description Of The Effluent Treatment System

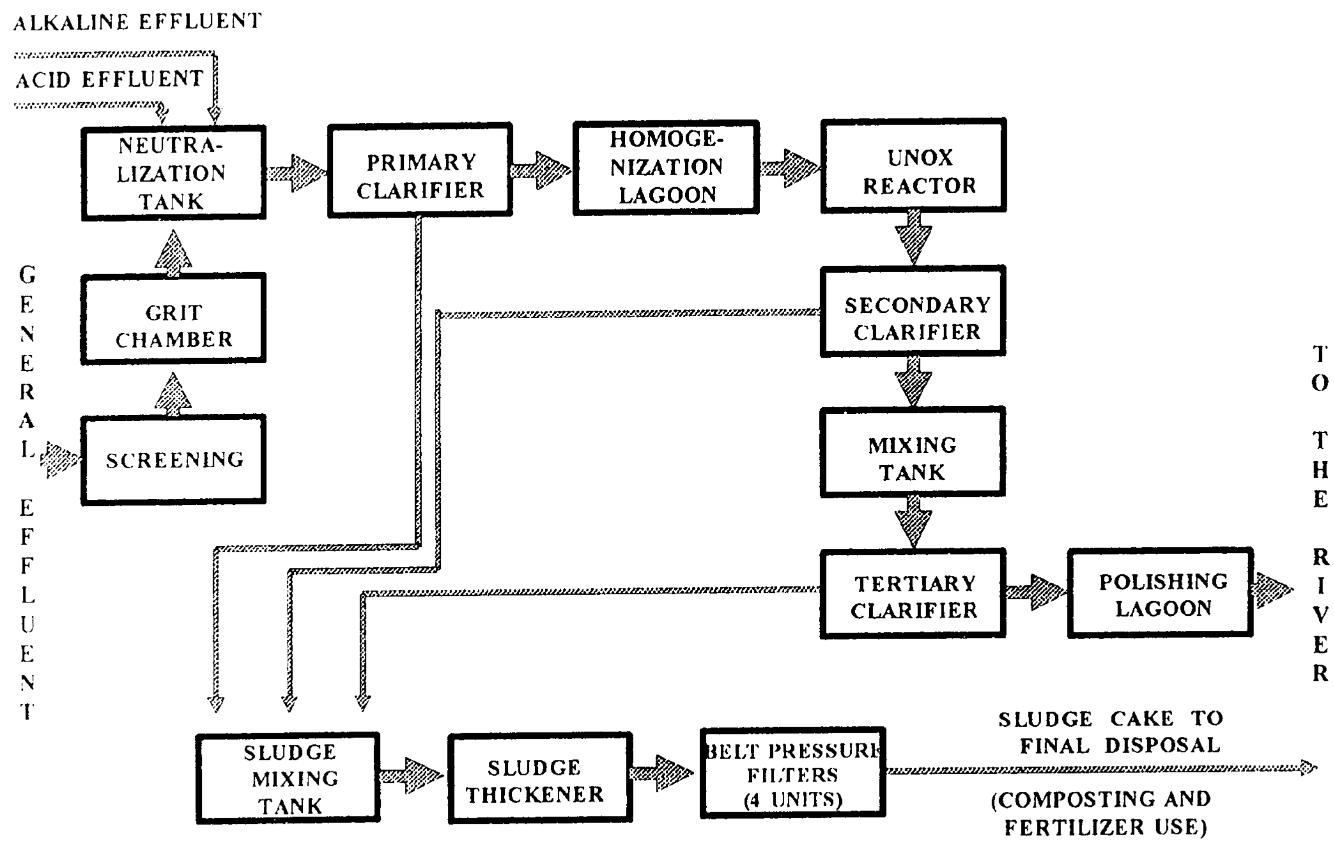
Effluents are treated at a tertiary level, using the best available technology. The plant started-up in 1982 and it is still one of the most advanced in the world pulp industry. The average flow per day is 38,000 m^3 and process water consumption is about 40 m^3/admt of products. All contaminated waters are included in this flow, and sanitary effluent was very welcome to it as source of microorganisms. Cooling waters, which have no risk of organic or chemical contamination, have separate flows and are monitored continuously for temperature, pH and conductivity.

The effluent treatment system is represented in the flow diagram and briefly described.

The effluents from the various areas, except the bleaching plant, are collected in underground pipelines and conveyed to the treatment plant by gravity. The general effluent passes initially through a screening system, a grit chamber, and going finally to a neutralization tank, which also receives the bleaching effluents. The neutralized effluent is fed to two settling clarifiers for suspended solids removal. After, it is cooled in heat exchangers to 37-38°C. Primary treatment comprises removal of solids, neutralization and cooling.

In case of any abnormal condition (high load, high chemical losses, high temperature, etc), the

FLOW DIAGRAM OF RIOCELL S.A. EFFLUENT TREATMENT PLANT



effluent is sent to an emergency lagoon, and later, after evaluation, it is gradually put back into the system. By this way, it is possible to prevent any harmful effect to the microorganisms in the secondary treatment.

After cooling, the effluent is homogenized in a lagoon with surface aerators and pumped to the Unox activated sludge reactor and secondary clarifiers. The system is an activated sludge treatment based on the use of oxygen to promote a more effective microorganism growth and action.

Riocell's choice for the Unox system was based on the fact that the available area for installing the plant was very small. Another advantage is the closed reactor, which avoids odor in the surroundings. Riocell is located near a huge community and odor problems must be minimum.

The biologically converted effluent is then sent to the tertiary treatment for color removal. This is achieved by flocculation with aluminum sulphate (alum solution) followed by sedimentation. Finally, the effluent is neutralized with lime, goes to a polishing lagoon and then pumped into the Guaiba river through diffusers.

Primary, secondary and tertiary sludges are thickened and dewatered in belt pressure filters. The sludge is bio-composted and converted in a valuable humus very demanded by local farmers.

Economical Considerations

Total capital investments to implement a concept like this today could reach US$ 45 million, representing 150 US$/admt year.

Major component in this cost are civil works (about 60-65%).

On the other hand, to operate the system, total costs reach about 10-12 US$/admt. Organic load measured as COD is about 50-65 kg/admt, being the major contributions those from bleaching plant (40%), pulp machine (20%), recovery boiler/evaporation (15%) and digester/washing (12%).

More than 50% of the total operational costs are due to the tertiary treatment (alum, pH correctors, defoamers, etc). Second most important cost comes from the secondary treatment, representing about 25-30% (oxygen, energy, urea, phosphoric acid, etc.).

Today Restrictions And Future Trends

Restrictions applied to Riocell's effluents are very strict. These limits have been set up by the State Environmental Agency before the starting up of the bleaching line in early 1980's. In some extent, they were the reason to go to tertiary level treatment.

Restrictions are based on concentrations and flow and not in pollution load, in opposition to a world-wide trend.

The State Environmental Agency argues that Nature is more concerned about pollutant concentrations instead of amount of pulp produced by the mankind.

For the sake of understanding, we are showing both ways, converting concentration in load, since effluent flow and production capacity are stable and relatively uniform.

At the same time, we are showing in the same table, Riocell's average figures for the year 1993.

Table 1 - Treated Effluent Quality Figures

Controlled Parameter	M=maximum m=minimum	Restrictions to Riocell ppm	Restrictions to Riocell kg/admt	1993 average figures kg/admt
COD	M	145	6.0	4.89
BOD_5	M	36	1.5	0.35
Suspended solids	M	45	2.0	0.69
Na, as NaOH	M	1050	50	40
Dissolved O_2	m	5	0.20	0.32
Oils/Greases	M	20	0.85	0.09
Total N_2	M	9	0.40	0.24
Chlorides	M	500	23	22.6
Phenols	M	0.05	0.0020	0.0011
Sulphides	M	0.18	0.0075	0.0036
Total phosphorus	M	0.9	0.040	0.023
Mercury	M	0.009	$4x10^{-4}$	0.1×10^{-4}
AOX	M	4.5	0.2	0.15
Color	--	no evidence of color		27.7
pH	--	6.0 - 8.5		6.6
Temperature	M	40°C		32-38

Although very restrictive, limitations are always becoming more and more tough.

There is another threat in Brazil to the high water consumption industries. Government, in the search to capture more money from tax-payers, is introducing taxation to the use of natural resources ("payer users") and fees to the discharge of wastewater to water streams ("polluter payers"). This is for sure a driving mechanism in the direction of closing the water cycle in the mills. This move is being very fast and there are no doubts that in few years taxations from environmental reasons may become a major issue in the production cost of pulp and paper. Riocell is anticipating to this threat by developing own technology to close the water cycle.

In relation to chlorinated organics, until now Riocell is being advised to run with AOX below 0.2 kg/admt. Dioxins and furans must be monitored in wastewaters and sludges. Samples are taken randomly and average figures are:

Table 2: Dioxin Figures

Wastewater (Treated Effluent)

2,3,7,8 TCDD	not detected (1 ppq d.l.)
2,3,7,8 TCDF	not detected (1 ppq d.l.)
Total toxic equivalent	0.3 to 1.3 ppq

d.l. = detection level

Sludge

2,3,7,8 TCDD	not detected
Total toxic equivalent	3 to 6.5 ppt

Chlorinated Organic Compounds

In 1988, when the "chlorine issue" was just gaining strength, Riocell decided to invest in an oxygen delignification, prior to the bleaching line. The reasons were the following: to reduce elemental chlorine consumption in the bleaching line, to reduce pitch problems in the system, and to raise the bleaching line capacity, since chlorine dioxide was bottlenecked.

At that time, the AOX figures in the final treated effluent were in the range 0.25 to 0.35 kg/admt. When the oxygen delignification came to work in 1990, the total active chlorine and caustic soda specific consumptions were reduced in about 40%. Overall raw effluent quality improved very much in terms of color and COD.

In 1991, the pulp industry was facing an enormous pressure from the greens because of the dioxin issue. Even fighting the shortage of chlorine dioxide to bleach the whole digester production, the mill started to increase the substitution rate at the first bleaching stage (Dc). Original project rate was 15% and today is 75-80%. In special runs, according to market requests, the mill runs ECF pulp.

In the new conditions, the AOX and dioxin figures were substantially reduced. AOX today is on the ranges: 0.4 to 0.7 kg/admt in the raw effluent, and 0.08 to 0.18 kg/admt in the treated effluent.

In tables 3 to 5, the typical figures for chlorinated compounds are shown. A blank sampling position for dioxin comparison was included. This point in the river is considered not to be polluted by any man-made source.

Table 3: Polichlorinated Compounds (Results in ppb)

Compounds*	Raw effluent	Treated effluent	Reduction %
2,4 dichlor phenol	9.8	n.d	100
2,4,6 trichlor phenol	0.9	n.d	100
2,3,4,5,6 pentachlor phenol	0.3	0.7	?
4,5 dichlor guaiacol	6.9	n.d	100
4,6 dichlor guaiacol	6.0	n.d	100
4,5,6 trichlor guaiacol	1.5	0.5	67
6 chlor vanillin	11.5	4.9	41
5,6 dichlor vanillin	0.5	n.d	100
3,4,5, trichlor syringol	2.8	1.6	39
3,4,5, trichlor cathecol	9.7	n.d	100
Phenols	11.0	0.7	94
Cathecols	9.7	n.d	100
Guaiacols	14.4	0.5	95
Vanillins	12.0	4.9	43
Syringols	2.8	1.6	39

* Other common phenols, cathecols, guaiacols, vanillins and syringols have not been detected.

Table 4: Dioxins In Raw And Treated Effluents (Detection Limit - 1 Ppq). Results In Ppq.

COMPOUNDS	Riocell's treated effluent	Guaiba river before Riocell	Guaiba river in a blank position	Drinking water
Tetrachlorodibenzodioxins	n.d.	39.1	n.d.	n.d.
Pentachlorodibenzodioxins	n.d.	7.1	n.d.	n.d.
Hexachlorodibenzodioxins	n.d.	n.d.	n.d.	n.d.
Heptachlorodibenzodioxins	69.0	18.4	71.3	8.4
Octachlorodibenzodioxins	255.5	201.4	554.1	131.2
Tetrachlorodibenzofurans	n.d.	44.4	n.d.	n.d.
Pentachlorodibenzofurans	0.4	17.5	n.d.	n.d.
Hexachlorodibenzofurans	O.9	1.6	n.d.	n.d.
Heptachlorodibenzofurans	O.5	n.d.	2.3	n.d.
Octachlorodibenzofurans	4.0	1.1	3.4	n.d.
2,3,7,8 TCDD	n.d.	3.2	n.d.	n.d.
1,2,3,7,8 PCDD	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8 HCDD	n.d.	n.d.	n.d.	n.d.
1,2,3,6,7,8 HCDD	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8,9 HCDD	n.d.	n.d.	n.d.	n.d.
1,2,3,4,6,7,8 HpCDD	69.0	9.5	36.4	3.5
2,3,7,8 TCDF	n.d.	2.1	n.d.	n.d.
1,2,3,7,8 PCDF	n.d.	1.0	n.d.	n.d.
2,3,4,7,8 PCDF	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8 HCDF	n.d.	n.d.	n.d.	n.d.
1,2,3,6,7,8 HCDF	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8,9 HCDF	n.d.	n.d.	n.d.	n.d.
2,3,4,6,7,8 HCDF	0.9	n.d.	n.d.	n.d.
1,2,3,4,6,7,8 HpCDF	n.d.	n.d.	2.3	n.d.
1,2,3,4,7,8,9 HpCDF	n.d.	n.d.	n.d.	n.d.
Total Toxic Equivalent	1.05	4.8	1.00	0.20

Table 5: Dioxins In Sludge And Sediments (Detection Limit = 0.5 ppt). Results In ppt.

Compounds	Riocell's sludge	River sediment before Riocell	River sediment in a blank position
Tetrachlorodibenzodioxins	73.1	10	3
Pentachlorodibenzodioxins	n.d.	10	2
Hexachlorodibenzodioxins	n.d.	26	4
Heptachlorodibenzodioxins	37.1	127	2
Octachlorodibenzodioxins	258.9	504	24
Tetrachlorodibenzofurans	112.5	12	3
Pentachlorodibenzofurans	n.d.	16	3
Hexachlorodibenzofurans	9.4	12	5
Heptachlorodibenzofurans	5.6	18	8
Octachlorodibenzofurans	19.4	25	3
2 3,7,8 TCDD	n.d.	n.d.	n.d.
1,2,3,7,8 PCDD	n.d.	0.7	n.d.
1,2,3,4,7,8 HCDD	n.d.	0.7	n.d.
1,2,3,6,7,8 HCDD	n.d.	3.4	0.5
1,2,3,7,8,9 HCDD	n.d.	1.7	n.d.
1,2,3,4,6,7,8 HpCDD	18.4	62.6	0.8
2,3,7,8 TCDF	18.7	1.3	n.d.
1,2,3,7,8 PCDF	n.d.	1.4	n.d.
2,3,4,7,8 PCDF	n.d.	0.8	n.d.
1,2,3,4,7.8 HCDF	7.5	1.6	0.6
1,2,3,6,7,8 HCDF	n.d.	1.5	0.7
1,2,3,7,8,9 HCDF	n.d.	n.d.	n.d.
2,3,4,6,7,8 HCDF	n.d.	0.6	n.d.
1,2,3,4,6,7,8 HpCDF	3.5	11.3	6.4
1,2,3,4,7,8,9 HpCDF	n.d.	n.d.	n.d.
Total Toxic Equivalent o.d. basis	3.1	3	~0

Treatment Efficiency And Projections For Improvement

Although very efficient, there is still room for further improvements. For better understanding of what happens along the several steps of treatment, the effluent is being deeply investigated (table 6). This enables us to discover losses we were not considering importants and to work for better results. For example, we became surprised with the so good efficiency of the primary treatment to reduce COD from 55 to 26 kg/admt. More careful investigations have proved the obvious: we were throwing to the sewer valuable fibers that could be recovered. An usual source of fiber losses is the centricleaner rejects.

Our aim now is to work in finding ways to completely close the water cycle. Certainly, this is an issue everybody is looking for.

It is our understanding we have partially solved the problem. As it can be seen in table 6, with a quintenary treatment, introducing two new steps in our today treatment system, we can reach a water with quality to be reused. The new steps are: filtration of the tertiary treatment in a sand bed filter and reverse osmosis. Both are well-known technologies. The filtration is very efficient to remove small micro-flocks and microorganism bodies, reducing color and COD.

There is still a key point to be solved: the recycling of reverse osmosis concentrated discharge liquid, containing all chlorides. Our efforts are now to find a purging point in the system to remove potassium and chlorides. All indications are to concentrate efforts in the recovery boiler fly-ash, very rich in these two elements.

Table 6: Total Effluent Free Mill Via Quintenary Treatment.

STAGE	kg / admt				
	Cl	-AOX	COD	BOD	COLOR
Raw Effluent	25	0.50	55	15	120
Settling	22	0.35	26	8	100
Activated Sludge	22	0.28	15	0.9	180
Flocculation / Settling	18	0.12	4	03	20
Filtration	18	0.10	2.3	0.25	13
Reverse Osmosis	1.5	0.002	0.25	0.1	0
Total Efficiency,%	94	99.6	99.5	99.3	100

Eco-Toxicological Evaluations

Bioessays are import quality control parameters. They are good indicators about treatment effectiveness and individual effluent contributions to the overall effluent.

The performed biological tests are: microtox (EC_{50}, acute toxicity); Daphnia similis (EC_{50}, acute toxicity); Ceriodaphnia dubia (toxic units, chronic toxicity), minows - Pimephales promelas (acute and chronic toxicities); and Ames test (Salmonella typhimurium, genotoxicity).

In terms of genotoxicity, both treated and raw effluent show no positive effects, better saying, they are not genotoxic according to Ames test.

Microtox test shows indications of toxicity in the raw and primary treatment effluents. Indication of toxicity means that we did not have 50% of affected individuals to calculate EC_{50}, but we had some toxicity. From secondary treatment onwards, we had no detectable microtox toxicity. The same trend is observed for Daphnia similis.

Chronic test with Ceriodaphnia dubia shows positive effect all over the treatment, although clearly reducing from raw effluent to the treated one. Usual way to express chronic toxicity is by the number of toxic units, that is obtained dividing 100 by the maximum concentration of the effluent which gives no observable effects, in percentage. Ideal figure is 1, when the concentration of nonobservable effects is 100%. This means, that even using 100% effluent, the microorganism grows as well as in the water blank.

For Ceriodaphnia dubia, usually the number of toxic units in the raw effluent is about 4 to 16, reducing to 1 to 4 in the treated effluent.

Till now, it was impossible to detect a real eco-toxicological difference between ECF runs effluent and standard production (75-80% substitution rate). However, there are strong indications that dissolving run effluents are more toxic, although showing much better figures for color, COD, BOD, etc.

Conclusion

Minimum environmental impact is not only to have nice quality control figures. It means a continuous effort in the direction of the zero impact. Closer you are to the zero, more difficult is to achieve your goal. However, this must be a philosophy, a conceptual way of working. In this way, Riocell feels proud to show its achievements, although we know there is still a lot to be done.

СЕЛСО ФОИЛКИЛ

Селсо Фоилкил - Технический директор Бразильской целлюлозно- бумажной ассоциации и Заместитель Президента Бразильской ассоциации целлюлозно-бумажных предприятий.

Господин Фоилкил - агроном со специализацией по лесоводству. Он закончил Сельскохозяйственный Университет Луиз де Квероз в Сао Паоло. Он получил диплом Мастера Наук по целлюлозно- бумажной промышленности в Университете охраны природы и лесоводству, в штате Нью-Йорк, Сиракуз.

Он был профессором в обоих университетах, в Сао Паоло и в Федеральном Университете Викоса. В настоящее время он является посещающим профессором в Федеральном Университете в Санта- Мария. В 1979 году, после четырёх лет работы в CENIBRA, он начал работу руководителем Технологического центра. В 1990 году он был назначен Директором по технологии и контролю по охране природы. В 1993 году под его руководством Технологический центр превратился в подразделение, приносящее прибыль.

CELSO FOELKEL

Celso Foelkel is technical director of the Brazilian Pulp and Paper Technical Association and vice-president of environment of the Brazilian Pulp and Paper Manufacturers' Association.

Mr. Foelkel is an agronomist with a major in Forestry. He graduated from the College of Agriculture Luiz de Queiroz of the University of São Paulo. He has a M. Sc. in pulp and paper technology, from New York State's College of Environmental Science and Forestry, Syracuse.

He has been a professor at both the University of São Paulo and Federal University of Viçosa. Currently, he is also a visiting professor at Federal University of Santa Maria. After working for four years with CENIBRA, he joined RIOCELL in 1979, as manager of the Technological Center. In 1990, he was appointed director of technology and environment. In 1993, the Technological Center was converted to a profit/business unit under his guidance.

PAPFOR 94 TECHNICAL CONFERENCE PROGRAM
10-12 October 1994
St. Petersburg, Russia

Monday, 10 October

0800-1000 Registration

1000-1030 **Current Status & Future Prospects for Pulp & Paper Industry in Russia**
V. Chuiko
Roslesprom

1030-1100 **Current Status and Future Prospects for the European Pulp and Paper Industry**
D. A. Clark
Confederation of European Paper Industries

1100-1130 Break

1130-1200 **Current Status & Future Prospects for the Ukranian Pulp & Paper Industry**
N. Lozovik
Ukraine Pulp and Paper Research Institute

1200-1230 **Current Status and Future Prospects for the Asian Pulp and Paper Industry**
K. Hata
Nippon Paper Industries Co., Ltd.

1230-1400 Lunch

1400-1430 **Current Status and Future Prospects for the Byelarus Pulp & Paper Industry**
V. Gavrilovich
Bellesbumprom

1430-1500 **Current Status and Future Prospects for the North American Pulp and Paper Industry**
M. Van Hook
American Forest & Paper Association

1500-1530 Break

1530-1600 **New Technologies and Equipment Proposed by the Russian Forest Company Technical Program**
O. Terentjev
St. Petersburg Technical University of Plant Polymers

Tuesday, 11 October

1330-1400 **Minimum Environmental Impact Via Riocell's Advanced Tertiary Level Wastewater**
C.E.B. Foelkel
Riocell S. A.

1400-1430 **Ecological Evaluation of the Modernization Project for the Baikal Mill**
V. Nevolin & A. Kryazhev
VNIIB
R. Zaikova
Baikal Mill
A. Beim
Institute of Toxical Ecology
W. Kalbfus
Bavarian State Institute for Water Research

1430-1500 Break

1500-1530 **Waste Dewatering and Utilization**
I. Gellman
National Council for Air and Stream Improvement

1530-1600 **Recycled Fiber Utilization**
R. J. Spangenberg
Weyerhaeuser Co.

Wednesday, 12 October

0900-0930 **Perspectives of Cellulose Composites for the Pulp and Paper Industry in the 21st Century**
E. Akim
VNIIB

1930-1000 **Pulping Processes Update**
T. J. McDonough
Institute of Paper Science & Technology

1000-1030 Break

1100-1130 **Alkaline Papermaking Possibilities for Russia**
H. Larsson
Eka Nobel Ab

Foelkel

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Научно-техническая
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