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ACTIVITY REPORT

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Improvement of
the Dephenolization Plant at the
RAS Kiviter Oil Shale Chemical Plant
Kohtla-Järve, Estonia

Dan Packy

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CONTENTS

Page

ABOUT THE AUTHOR iii
ACRONYMS AND ABBREVIATIONS v
EXECUTIVE SUMMARY vii

CHAPTER 1: INTRODUCTION 1

1.1 Overview 1
1.2 Objectives 1
1.3 Study Activities 1
1.4 Schedule 2
1.5 Budget 2

CHAPTER 2: PROCESS DESCRIPTION OVERVIEW 3

2.1 Introduction 3
2.2 Extraction 3
2.3 Steam Stripping 4
2.4 Solvent Regeneration 4
2.5 Process Information 5
2.5.1 Plant Design 5
2.5.2 Plant Performance Indicators 5
2.5.3 Plant Cost Performance 6

CHAPTER 3: CONCLUSIONS 7

3.1 Distillation Column Reboiler Steam Consumption 7
3.2 Distillation Column Phenol Degradation 7
3.3 Solvent Breakdown 7
3.4 Number of Actual Extraction Stages 7
3.5 Overall Extraction Column Performance 7
3.6 Influent and Effluent Phenol Concentration 8
3.7 Separation/Purification System Vacuum System 8
3.8 Separation/Purification System Overhead Condenser 8
3.9 Physical Separation between Dephenolization Plant and Phenol Purification Plant 9

CHAPTER 4: RECOMMENDATIONS 11

4.1 Capital Improvements 11
4.1.1 Solvent Regeneration Column Reboilers 11
4.1.2 Extraction Column Interface Measurement and Control 11

4.2 Process Technology Changes 12
4.2.1 Two-Stage Solvent Extraction 12
4.2.2 Use of a Secondary Solvent 12
4.2.3 Vacuum Distillation for the Steam Stripping Column 12
4.2.4 Vacuum Distillation for the Second Solvent Regeneration Column 12

TABLES

1. Schedule for Improvement/Optimization Study 2
2. Reboiler Information 13
3. Interface Instrument Summary 14

ABOUT THE AUTHOR

Daniel V. Packy is a Senior Staff Chemical Engineer and Project Manager in Radian Corporation's Herndon, Virginia, office. He currently provides technical support to several companies in the chemical and manufacturing industries for compliance with various environmental regulations. Mr. Packy has also designed and supervised the construction of several remediation projects. Prior to joining Radian, he served in engineering management, design engineering, and production supervision roles for a major manufacturer in the chemical process industry.

ACRONYMS AND ABBREVIATIONS

EEK	Estonian crowns
EHP	Environmental Health Project
m3/hr	square meters per hour
mw	megawatt

EXECUTIVE SUMMARY

The Environmental Health Project (EHP) team has conducted an improvement/ optimization study of the dephenolization plant at the RAS Kiviter oil shale chemical plant located in Kohtla-Järve, Estonia. The objectives of the study were to identify items to:

- Improve the economic performance of the plant by achieving higher phenol product yields and reducing operating costs.
- Improve the environmental performance of the plant by reducing the phenol loading in the wastewater effluent to the RAS Kiviter treatment facility.

From the results of plant visits and preliminary engineering studies, the team recommends that two capital improvements and four process studies be implemented. The capital improvements are:

- replace existing reboilers for the two solvent regeneration distillation columns; and
- purchase new interface level indicators and controls for the extraction columns.

The team further recommends that Dr. Leevi Molder be subcontracted to conduct process studies on the following four areas:

- investigate two-stage extraction using butyl acetate and isopropyl ether solvent;
- use a secondary solvent to extract butyl acetate from the water stream;
- investigate applying vacuum to the steam stripping column to reduce steam load; and
- investigate applying vacuum to the second solvent regeneration column to improve separation and product quality.

The EHP team anticipates that implementing these recommendations will lead to improving the plant's economic performance and reducing its environmental impact. The capital improvements may lead to approximately 1,700,000 EEK/yr (US $150,000/yr) savings in steam costs and may improve the yield of phenols by 22,000 kg/year at a value of approximately 250,000 EEK/yr (US $22,000/yr). The additional phenols yield also reduces the phenols loading to the RAS Kiviter wastewater treatment plant by an equal amount.

With concurrence from RAS Kiviter, the EHP team will begin implementing these recommendations so that they can be completed by September 1996.

1 INTRODUCTION

1.1 Overview

The U.S. Agency for International Development (USAID), through the Environmental Health Project, is providing assistance to the RAS Kivitier oil shale chemical plant located in Kohtla-Järve, Estonia. EHP's activities are intended to reduce the environmental impacts of RAS Kiviter's processes and contribute to the financial viability of the facility. One of the tasks undertaken by EHP is to identify markets for the phenol-based compounds and to improve the performance of the the dephenolization plant. During Phase I of the activity EHP assistance on this task concentrated on developing markets for phenolic compounds to provide Kiviter an incentive to produce more phenolic products. This report recommends steps to improve the performance of the dephenolization unit.

1.2 Objectives

The objectives of the phenols products market development task are to:

- Identify new product application markets for the phenol-based compounds RAS Kiviter currently produces, and
- Improve the performance of the dephenolization plant.

EHP conducted an improvement/ optimization study to investigate ways to improve the dephenolization plant's performance, which includes increasing product quality, decreasing plant production costs, and reducing phenols in the plant effluent water.

By improving plant performance to recover more phenol and reduce operating costs, RAS Kiviter should be able to improve its manufacturing position of these valuable chemical intermediates. Coupling an improved manufacturing position with new potential market applications may then improve RAS Kiviter's economic viability. In addition, recovering more phenol from the wastewater stream will reduce pollutant loading to the RAS Kiviter wastewater treatment plant, allowing better operation of that process and reducing the overall environmental impact of the entire oil shale chemical plant.

1.3 Study Activities

The improvement/optimization study consists of the following four activities:

- Visit the RAS Kiviter plant to obtain information on the dephenolization plant operation, current restrictions, and existing improvement ideas, and to potentially develop additional improvement ideas.
- Conduct preliminary engineering to evaluate the feasibility of the identified improvements.
- Generate recommendations regarding the improvements and obtain approval for the recommendations from all involved parties.
- Implement the recommendations, including purchase, installation, and start-up of new equipment, by September 1996.

1.4 Schedule

Table 1 provides the overall schedule for the improvement/optimization study. More detailed schedules with milestones for the implementation will be developed after the results of the study are accepted and more detailed engineering is underway.

1.5 Budget

The budget for the improvement/optimization study includes funding for both labor and capital purchases. In the original scope of work for the phenol products market development task, the following budgets were established for the dephenolization improvement/optimization subtask:

U.S. labor days:	44
Estonian labor days:	30
Commodities (approximate):	US $130,000

The budget for commodities may be increased depending on the success of the other tasks.

Table 1

Schedule for Improvement/Optimization Study

Activity	Schedule
Site visit to RAS Kiviter	December 1995
Preliminary engineering	January 1996
Draft study report	January 1996
Final study report/approval	February 1996
Implementation	March-September 1996
Project completion	September 1996

2 PROCESS DESCRIPTION OVERVIEW

2.1 Introduction

At the RAS Kiviter facility, oil shale is heated in retorts to release gas, condensibles, and shale oil as overhead streams, with semi-coke exiting as a bottoms stream. The overhead condensibles stream is quenched with water. The water-soluble phenols partition to the water while oil-soluble phenols remain in the condensed oil phase. The water-soluble phenols in the water phase are directed to intermediate storage tanks and then to the dephenolization plant.

The dephenolization plant removes the mixed phenols from the predominantly water stream. After the phenols are removed, the water is sent to the RAS Kiviter wastewater treatment plant for biological treatment before being discharged to surface water, which eventually reaches the Gulf of Finland. The plant uses liquid-liquid extraction, steam stripping, and distillation to separate the phenols from the water.

Butyl acetate is currently used as the solvent to remove the phenols from the water stream. The phenol-laden butyl acetate is then regenerated and continuously recycled within the plant. The phenols are removed from the solvent and concentrated by distillation. The concentrated phenols can then be sent to a phenol purification plant, which is physically located approximately 1 kilometer from the dephenolization plant. In the phenol purification plant, the concentrated phenols can be fractionated by a batch distillation process.

The dephenolization plant consists of two parallel equipment trains (known as Line 1 and Line 2) that were originally designed for a throughput of 160 m^3/hr. Currently, because of reduced retort production, only one train operates at any one time, at an influent water flow rate of 30-45 m^3/hr.

Each of the parallel trains consists of the following major equipment:

- four vertical liquid-liquid extraction columns;
- one steam distillation column; and
- two solvent regeneration distillation columns.

Each train also includes several storage tanks, heat exchangers, reboilers, and condensers with the distillation columns, as well as one additional column used as a vent scrubber.

2.2 Extraction

Each extraction train consists of four vertical liquid-liquid extraction columns. The columns operate in series, with the solvent and water flowing in a countercurrent mode. Water is admitted to the top of each column through a distributor and then flows downward by gravity. Solvent enters the bottom of each column, also through a distributor, and flows upward because of its lower specific gravity compared to water. The water is withdrawn from the bottom of the column, below the solvent distributor, while solvent is withdrawn from the top of each column, above the water distributor.

The extraction columns are all 2 meters in diameter and vary in height between 21.5 and 30 meters. They are constructed from carbon

steel, are uninsulated, and do not contain any packing. The columns have differential pressure, bubbler-type instrumentation to monitor and control the water/solvent interface.

During the visit, Line 2 was operating, while Line 1 was mostly undergoing a maintenance overhaul, including replacement of one extraction column. To improve the liquid-liquid extraction process, the first (and tallest) column from the Line 1 train was actually in use with the remainder of the Line 2 train, so that the current process actually uses five columns in series.

Existing instrumentation to monitor the interface level in the extraction columns consists of a pneumatic, bubbler-type system. In the system, two tubes are installed in each column from the top and extend approximately halfway down the column. One tube is approximately 2 meters longer than the other tube. The desired interface is approximately midway between the ends of the two tubes. Controlled, pressure-regulated air is admitted to each tube to establish a slight flow of air through the tubes. The back-pressure in each tube is monitored and compared by a differential pressure sensor. The measured differential pressure corresponds to the density of liquid and the vertical difference between the submersed ends of the two tubes. Because the liquid density in the vertical distance between the tube ends varies as the interface changes, the measure differential pressure also corresponds to the solvent/water interface.

The interface measurement devices provide input signals to the flow controller for the bottom outlet water stream on each column. The entire loop consists of pneumatic instruments, except for mechanical/electric strip chart recording of the flow rate.

2.3 Steam Stripping

After the water exits the last extraction column, it is fed through heat exchangers to a steam stripping column. The column removes additional phenols and some solvent from the water. The cleaned water exits through the bottom of the column, flows through heat exchangers to recover heat, and then flows to a storage tank. From there, the water flows to the wastewater treatment plant.

Steam to the distillation column is a combination of high-pressure condensate from the solvent regeneration columns after pressure reduction and flashing, and make-up steam. The distillate from the column is combined with regenerated solvent and returned to the extraction train. The column operates at atmospheric pressure and has no reflux.

The steam stripping column is also 2 meters in diameter but is 19 meters tall and includes 12 trays. It is insulated and includes typical stages of heat recovery and interchange between feed, distillate, and bottoms streams.

2.4 Solvent Regeneration

Two atmospheric distillation columns, arranged in series, are used to reconcentrate the butyl acetate solvent and separate the mixed phenols from this solvent. The first distillation column receives the phenol-laden solvent from the first (dirtiest) extraction column. Facility steam, at a pressure of approximately 30 atmospheres, is fed to a horizontal tube reboiler, to supply the heat required for the distillation. Approximately 80 to 90% of the butyl acetate that is recovered in the process, with a small amount of water and phenols, goes overhead. The remaining butyl acetate, with a high concentration of phenols, exits from the reboiler and is fed to the second

column. The amount of butyl acetate recovered in the first column depends on the solvent/water ratio. Steam condensate from the reboiler is collected, flashed at lower pressure, and returned to the steam stripping column.

The first column is 2 meters in diameter and 22 meters tall and contains trays. It is also insulated and includes typical stages of heat recovery and interchange between feed, distillate, and bottoms streams.

The second distillation column receives the remaining butyl acetate/phenols stream from the first distillation column. Facility steam, at a pressure of approximately 13 atmospheres, is fed to a horizontal tube reboiler to supply the heat for distillation. Because of the age and condition of the equipment, steam is also admitted directly to the column to supply additional energy. The phenols concentrate as the unit product in the bottom phase of the second column while clean butyl acetate goes overhead.

The second column is 0.6 meters in diameter and 20 meters tall and contains rasching rings. It is also insulated and includes typical stages of heat recovery and interchange between feed, distillate, and bottoms streams.

Butyl acetate is the overhead stream from both columns. It is combined and returned to the extraction columns. The phenols product is withdrawn from the bottom of the second column and is either transferred to the phenol fractionation area for further processing or combined with the oil product from the retorts when it is not needed as product.

2.5 Process Information

General information on plant design and performance obtained during the visit is provided below.

2.5.1 Plant Design

Original design capacity:
130 m^3/hr influent water flow

Current operating rates:
30-45 m^3/hr influent water flow, into one line. Only one line typically operates at one time; typical throughput is 27,000 m^3/month

Typical phenol concentration:
10-11 g/l phenols in influent
0.3 g/l phenols in effluent
0.7 g/l limit for phenols in effluent

Solvent:
butyl acetate, currently (previously, a mixture of butyl acetate and di-iso-propyl ether)

Solvent/liquid ratio:
Variable from 8%-30% solvent to water, depending on solvent used and degree of extraction desired; currently using 12% with butyl acetate solvent; need to go to 30% if mixed butyl acetate/di-isopropyl ether is used

2.5.2 Plant Performance Indicators

Steam consumption:
5 to 8 metric tons/hr
120 mw/day (theoretical minimum)
150 mw/day typical
200 mw/day prior to 5th extraction column use

Total rectification steam use: 5 tons/hr

Solvent consumption:
10-15 tons/month

Solvent usage:
80 kg butyl acetate/ton phenol produced

2.5.3 Plant Cost Performance

Although detailed information regarding plant finances was not provided, the following information was obtained.

Main unit costs:
60% of total, steam
20% of total, butyl acetate
20% of total, all other costs

Steam costs:
800,000-1,000,000 EEK/month

Steam costs:
190 EEK/mw-hr (regardless of pressure)

Solvent costs:
Butyl Acetate: 18,000 EEK/ton
Di-isopropyl ether: 22,000 EEK/ton

3 CONCLUSIONS

During several plant visits, members of the EHP team met with RAS Kiviter operating personnel and Dr. Leevi Molder and toured the dephenolization plant. These meetings identified several areas of the plant that limit or restrict production. These areas and their impact on production are described below.

3.1 Distillation Column Reboiler Steam Consumption

The solvent regeneration column reboilers are approximately 35 years old and no longer operate at their design pressure. They consume more steam than necessary to effect the separation, increasing plant operating costs.

3.2 Distillation Column Phenol Degradation

The current reboilers are horizontal, kettle-type heat exchangers with bayonet-type tube bundles and are not designed to handle nonstable organic liquids. Because of their design, they overheat the bottoms product, which degrades the concentrated mixed phenols from high molecular-weight, more valuable constituents to low molecular-weight, less valuable products. This overheating therefore reduces the quality and economic value of the final product.

3.3 Solvent Breakdown

Sampling data indicate that the butyl acetate solvent breaks down in the first solvent regeneration column, creating butyl alcohol and acetic acid. This breakdown reduces the solvent's ability to remove phenol from the water stream, creates a low boiling azeotrope in the steam stripping column that reduces the wastewater effluent quality, and causes corrosion in the solvent regeneration column heat exchangers. All of these problems reduce the plant's ability to separate and recover phenols.

3.4 Number of Actual Extraction Stages

The extraction columns operate in series to remove phenols from the water stream. The number of theoretical stages of extraction that the columns achieve varies from 5 to 8. The number of stages achieved partially depends on the control of the water/solvent interface level that exists in each column.

Although the columns have interface measurement instrumentation, it does not currently operate. The control valves also do not function properly to meter the flow of water and solvent from the columns. Personnel collect grab samples from several taps on the columns to obtain a rough approximation of the location of the interface. This limitation restricts their ability to operate the columns efficiently and thus reduces the plant's ability to separate phenols from the water stream.

3.5 Overall Extraction Column Performance

The performance of the extraction columns is limited because of their overall design, the lack of packing that would promote contact between the two liquid phases, and the

lack of temperature control (the columns are outdoors and uninsulated) needed to achieve the most efficient extraction temperature. Other liquid-liquid extraction technologies and equipment are available to solve some or all of these problems. Potential alternative equipment is described below.

Centrifugal Extractor

Alfa Laval manufactures a centrifugal extractor which uses a motor-driven, high-speed rotating bowl to provide phase-to-phase contact and provide for the liquid-liquid extraction. Personnel have met with representatives from the manufacturer to discuss the feasibility of this type of equipment in this application. Additional bench- and pilot-scale study is required.

Rotating Extractor

Plant personnel are also investigating the use of a rotating extractor, a column-shaped vessel with slowly rotating internal agitators that would improve the phase-to-phase contact between solvent and water and therefore provide better extraction. Again, additional study is required to evaluate the feasibility of this equipment.

3.6 Influent and Effluent Phenol Concentration

The influent water stream normally contains 10-15 grams/liter of dissolved mixed phenols. However, personnel cannot continuously monitor the phenol concentration of the influent water and therefore cannot adjust the plant flow rates, solvent-to-liquid ratios, and steam flow rates to optimize performance. The degree of phenol separation is therefore below optimum.

The effluent water stream normally contains 300 milligrams/liter of dissolved mixed phenols. Again, personnel cannot continuously measure the phenol concentration of this effluent, so they cannot evaluate actual performance. In addition, because they cannot determine if a process upset occurs and causes an increase in the effluent phenol concentration, they cannot take measures to counteract the upset, redirect the effluent, and minimize impact on the wastewater treatment plant.

3.7 Separation/Purification System Vacuum System

The equipment used to produce vacuum for the phenol purification process is energy inefficient and no longer achieves the desired vacuum. The steam jet ejectors were designed to use plant steam at a supply pressure of 13 atmospheres to develop the required vacuum of 1 torr. However, the ejectors can now only accept 6 atmosphere steam and achieve a vacuum of 10 torr. These restrictions lead to reduced capacity and lower quality for the phenol purification plant.

3.8 Separation/Purification System Overhead Condenser

The current overhead condenser for the phenol purification columns leaks because of mechanical problems. The condenser was apparently not designed to handle the thermal expansion that occurs during operation. Water leakage into the system reduces the final quality of the separated phenol products.

3.9 Physical Separation between Dephenolization Plant and Phenol Purification Plant

The dephenolization plant is currently located approximately 1 kilometer from the phenol purification plant. Because of the high

freezing point of the phenol/solvent feedstream (originating from the bottom of the second solvent regeneration column), it is difficult to transfer this stream between the two plants without freezing or decomposition of the phenols. This decomposition also reduces the quality and economic value of the final product.

4 RECOMMENDATIONS

Based on the results of the plant visits, the EHP team recommends that up to two capital improvements and four process studies be implemented. The capital improvements include purchasing new or replacement items to improve plant operation and reduce cost. The process studies include investigation by Dr. Leevi Molder on ways to improve the overall process for greater product quality and reduce phenol in the water effluent.

4.1 Capital Improvements

4.1.1 Solvent Regeneration Column Reboilers

The EHP team recommends that the solvent column reboilers be replaced with new units. The new units should be a falling-film evaporator design and should be specified for the flow rates, process vacuum, and steam pressure ratings necessary for the current solvent regeneration process.

Replacement reboilers will reduce the steam consumption of the solvent regeneration columns. Based on preliminary engineering and cost calculations, the potential reduction in steam consumption using new reboilers will be approximately 25%. This amounts to 2 metric tons of steam per hour at an approximate annual savings of 1,700,000 EEK/yr ($150,000/yr). In addition, falling-film evaporators will also reduce the degradation of the concentrated mixed phenols in the column bottoms streams, thus improving the final product quality of the unit.

Using basic design parameters obtained from RAS Kiviter personnel, EHP team members contacted U.S. manufacturers of falling-film evaporators to investigate costs. Table 2 provides information regarding significant design parameters and vendor quotes for these heat exchangers.

4.1.2 Extraction Column Interface Measurement and Control

The EHP team recommends that new instrumentation be purchased to replace the existing interface indicators and controllers. The existing bubbler-type interface measurement devices do not function properly. In fact, most of the devices have been removed and are being repaired. The control valves that meter the flow also do not function properly. New equipment to measure the solvent/water interface and control the solvent and water flow will improve the operation of the extraction columns and improve the phenol separation capability of the plant.

Based on preliminary calculations, improvements in level control of the extraction columns may lead to reducing the effluent phenol concentration approximately 0.1 grams/liter. This reduction in effluent concentration translates to an additional recovery of phenol product of 22,000 kg/yr at a savings of 250,000 EEK/yr (US $22,000/yr) and an equivalent reduction in phenol loading to the RAS Kiviter wastewater treatment plant.

Table 3 summarizes the contacts the EHP team made with various U.S. vendors of level instrumentation and control systems. Of the contacts made, only one can provide a replacement bubbler-type system. The others all recommend using other technology (e.g.,

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capacitance or viscosity) to sense the solvent/water interface. Additional engineering will be required to select the best replacement instruments.

4.2 Process Technology Changes

The four recommended additional process studies to be conducted by Dr. Leevi Molder are described below. The EHP team recommends that "local" Estonian contractor funds under the Phase II phenols task be used to fund some or all of these process studies.

4.2.1 Two-Stage Solvent Extraction

The plant currently uses butyl acetate because of its lower purchase cost and its ability to extract phenols at lower solvent/liquid ratios. However, the use of a mixed solvent would provide better extraction. Dr. Molder coauthored a technical paper describing the use of a two-stage extraction process, using a mixed butyl acetate/isopropyl ether solvent, with each stage having separate extractant cycles. Additional bench-scale testing is required to determine the viability of this process.

4.2.2 Use of a Secondary Solvent

The use of a secondary solvent such as benzene to extract the residual butyl acetate from the water may lead to lower overall energy costs than the current process. This concept has also been investigated but would require more study to evaluate its viability.

4.2.3 Vacuum Distillation for the Steam Stripping Column

Applying vacuum to the steam stripping column would reduce the steam requirements on this column and improve the removal of residual phenol from the wastewater. Additional study is required to evaluate the potential benefits versus costs.

4.2.4 Vacuum Distillation for the Second Solvent Regeneration Column

Applying vacuum to the second solvent regeneration column would also reduce the steam requirement to this column and may improve the mixed phenol product quality. Operating under vacuum would allow lower operating temperatures, which in turn reduces the phenol degradation. Again, additional study is required.

Table 2

Reboiler Information

Item #	Equipment	Heat Transfer Coefficient U $\frac{Kcal}{m^2 - hr - °C}$	Heat Transfer Area (m^2)	Heat Transfer Duty (Kcal/hr)	Capital Cost
T-4:	First Column Reboiler	500	90	2×10^6	$55,000
T-5:	Second Column Reboiler	250	25	0.5×10^6	$21,000

Table 3

Interface Instrument Summary

Manufacturer	Type of Equipment	Response	Recommendations	Purchase Cost
Uehling Instruments	differential pressure bubbler	can provide replacement system	quotation supplied	$2,300 per tank, delivery 1-2 weeks
Delta Controls	differential pressure probes	suggest alternate technology	suggest direct sensing differential pressure indicators	$2,500 per tank
Dynatrol	viscosity probes	suggest alternate technology	suggest viscosity probes as switch and alarm points	US $13,000 per tank, for two viscosity-based switch indicators
Fluid Components	thermal dispersion probes	suggest alternate technology	suggest thermal conductance probes as switch and alarm points	US $1,500 per tank, for two thermal conductance-based switch indicators
Dwyer Controls	differential pressure sensors	suggest alternate technology	tank mount differential pressure probes to sense density changes	US $500 per tank, only for sensors, needs additional controls
Magnetrol	float-type buoyancy/density indicators	suggest alternate technology	top mounted float descends to sense density at solvent/water interface	