The technological Aspects of Liquid Radioactive Waste Treatment - 8353

Tibor Krajc, Marian Stubna, Milan Zatkulak
VUJE, a.s.
Okruzna 5, 918 64 Trnava, Slovak Republic

Martin Slezak, Vladimir Remias
JAVYS, a.s.
919 31 Jaslovske Bohunice, Slovak Republic

Abstract

The Final Treatment Center (FTC) at Mochovce Nuclear Power Plant (NPP) have been tested with radioactive medias during commissioning phase (02 - 04/2007) and then introduced to trial operation in 10/2007. One-year trial operation of facility is planned.

This paper introducing the short description of FTC technological equipments and the description of technological procedures including the basic technological parameters of both used technologies.

The paper is dealing with the description and commentary of inactive/model testing phase and the radioactive test phase, too. A commentary to trial operation preparation works is given.

The evaluation of experience gained in the phases of Center commissioning and partially trial operation as well is a part of this paper.

The identification of key interdependences within process parameters and treatment product properties is carried out.

The fulfillment of the projected output parameters for all technological facilities and the achievement of required qualitative parameters of individual treated RAW products are displayed.

1. INTRODUCTION

The Final Treatment Center (FTC) in Mochovce is designed for the treatment of liquid radioactive wastes (concentrates, spent resins with sludge) originated from NPP Mochovce operation and for solid radioactive wastes' expedition to Bohunice Treatment Center (BTC), too. In addition to this the grouting of drums with waste treatment product from Bohunice with radioactive cement waste product is allowed as well.
So, the 200dm^3 steel drums with bitumen product or BTC treatment products placed in Fibre Reinforced concrete containers (FRC) and grouted with cemented overconcentrate are used for disposal of waste treatment products in the National Radioactive Waste Repository at Mochovce.

2. DESCRIPTION OF FINAL TREATMENT CENTER MOCHOVCE

2.1 FTC capacity

FTC is operating on a campaign schedule. Five campaigns of bituminization of concentrates and one campaign of bituminization of resin and sludge are planned per year.
Cementation campaign follows after each bituminization campaign.
So, the overall capacity of FTC for concentrates is 870m^3/year and for spent resin and sludge mixture is 40 m^3/year (1.205 drums with bitumen product and 172 filled FRC containers).

2.2 Description of technological procedures

The technology of bituminization on Thin Film Evaporator is installed for the treatment of radioactive concentrates. The bituminization of spent resins and sludge is carried out on discontinuous batch type facility. This facility is consists of decanter, dryer and mixer-homogenizer. 200dm^3 steel drums are used for the collection of bitumen product in both technologies. The bitumen products in drums are putted, after temporary storage into FRC containers (7 pieces/container) and are grouted by cement product.
The cement grout is prepared by mixing of overconcentrate (salt content: 400-450 g/dm^3) with lime and zeolite-cement mixture. The overconcentrate is prepared by evaporation on circulation steam heated evaporator. After the solidification of cement grout the lid of container and the plugs will be sealed by fibre reinforced cement mixture.

2.2.1 Bituminization of concentrates

Adding concentrated nitric acid in order to adjust the pH value modifies the concentrate originated from Auxiliary Building (AB). After preheating the processed concentrates are dosed mutually with bitumen to a Thin Film Evaporator (TFE) at the same time. The feeding rate of concentrate and bitumen is adjusted in order to obtain the bitumen product with salt content 40% (w.)
The bitumen product is discharged from the bottom nozzle of the evaporator into 200dm^3 steel drum. The drums are automatically capped and the activity of ^{137}Cs a ^{60}Co is measured.

2.2.2 Bituminization of resins and sludge

The suspension of spent resin and sludge mixture has transported from AB into receiving FTC tank. The suspended spent resins and sludge mixture is pumped into a decanter.
The sediment is isolated in decanter from water phase and consequently flows down by gravity into the dryer heated by steam.
The dried sediment of spent resins and sludge is mixed with melted bitumen in batch type mixer equipped with rotating blades. After gradual adding of sediment and short mixing the mixture is the bitumen product discharged to 200 dm^3 drums similarly like bitumen product from TFE. The ratio of bitumen-sediment-Polyethylene is adjusted in order to achieve the 40 % (w.) portion of resins and sludge in bitumen product.

2.2.3 Production of overconcentrate and cement grout

The overconcentrate is prepared using recirculation evaporator. The dosing rate of concentrate and the flow-rate of heating steam are adjusted in accordance with the required overconcentration. The salt concentration in output stream is up to 400 g/dm^3. Concentrates are taken from the cyclone separator at the top part of the evaporator and collected in a concentrate's storage tank provided with mixer and is heating to keep the temperature of concentrates above 40 °C. The overconcentrate is pumped from storage tank to a cementation line’s feeding tank.

The cement grout is prepared from overconcentrate by mixing with lime and cement blended with zeolite.
A FRC container loaded with bitumen product drums or drums originated from BTC is then filled with cement grout dosed by pump.
The filled FRC containers are cured on roller conveyor and the plugs are sealed using fibre reinforced concrete mixture.
This container meets all limits for final disposal so after checking procedure, it is transported to the National Radioactive Waste Repository at Mochovce.

3. Description of tests performed.

3.1 Model (inactive) test phase Description and Commentary.

3.1.1 Objective of the test

After the execution of individual system parts testing (pre-complex tests) the complex tests were performed in order to verify the technological equipment quality from the point of view the complex check of operation ability of all systems in the model test conditions.

3.1.2 Overview of model tests

On the strength of the successful pre-complex checkouts, and after the readiness of the equipment and the staff had been confirmed, the inactive complex checkout of technologies for treatment and conditioning RAW in FTC started.
The inactive complex checkouts were in progress from 18th of September 2006 to 8th of November 2006. During these tests the technologies of bituminization of concentrates, resins and sludge into 200dm^3 steel barrels were examined. Moreover, all the operating and transport means dedicated to the manipulation with steel barrels, including their deposition into the Cubical Fibre Reinforced Concrete Containers were tried out.
In the same way, the recirculation evaporator for preparation of overconcentrate and the cementation line for cement grout production were equally examined. The cement grout was used to embed the free space among the barrels in Cubical Fibre Reinforced Concrete Containers.
Inactive simulators of liquid RAW that had been prepared directly in the operational tanks of FTC were used.
Approximately 7m^3 of model concentrate that simulated the composition and properties of the radioactive concentrate from the NPP EMO was applied. Circa 470 kg of dried spent resins together with 200 kg dried sludge were mixed with 12m^3 de-mineralized water and used to prepare the inactive suspension of resins. Because of limited capacity of the storage tank for resins and sludge (max. 7,5m^3) this suspension was prepared in two parts. The tests of individual technologies were realized in the following time sequence:

1. In-active test of bituminization of concentrates
2. In-active test of bituminization of resins and sludge
3. In-active test of the recycle evaporator
4. In-active test of cementation

The purpose of these tests was to give proof of the functionality of individual technologies in non-radioactive conditions as well as the functionality of the whole system FTC in Mochovce.
The time sequence started from the designed state when at first the reserve of the bitumen product in 200dm^3 barrels is created. These barrels are temporary warehoused in the

determined area of FTC and then the barrels are deposited into Cubical Fibre Reinforced Concrete Containers (7 barrels in every FRC). Then the container is closed and prepared for the next operation – the embedding of the free container space. Before the drums in FRC are embedded, the reserve of overconcentrate is prepared to fill the free volume (approx. 1,5m^3). When the FRC is filled it is sealed and after the sealing and the packing is mature it is ready for transport to the final disposal facility.
During the test some technical faults and drawbacks that did not allow continue the tests according to the planned schedule appeared. The tests were realized operatively according to the actual plan of individual technologies, let us say according to the state of the defects and drawbacks elimination. At last all the planned tests were realized according to the program. The result of the non-active test is the number of 3 FRC containers with steel barrels containing bitumen product were inserted. The free space in the containers was embedded with 9 sealing dosages of simulator made of cement sealing.
The recommended parameters for radioactive test performance were specified on the basis of model tests evaluation. The results of model test served as a basis for authorization of radioactive test execution, too.

3.2 Radioactive test phase Description and Commentary.

3.2.1 Bituminization of concentrates

Objectives of complex active tests for concentrates bituminization on TFE:

1. Test of radioactive concentrates and bitumen pumping to operational tanks
2. Test of pH value adjusting, circulation pumping and mixing, temperature adjusting in automatic regime
3. Test of radioactive concentrates dosing from operational tank to TFE
4. Test TFE operation
5. Test of condensate cleaning
6. Test of drum filling, capping procedure and gamma scanning
7. Test of supporting systems: heating steam supply, cooling water supply and air conditioning system

Criterions of successful complex test:

1. Successful repumping of radioactive concentrates to operational tank
2. Production of **5** drums with bitumen product at concentrate injection rate 200 kg/h
3. Value of salt content in bitumen product ≥ 40% (W.)
4. Residual water content in bitumen product < 1% (W.)
5. Successful repumping of distillate from FTC to AB
6. Oil content in condensate < 50mg/dm^3, evaporation residue <200mg/dm^3)

9.1m^3 concentrate with salt content (before pH value modification) 153 g/dm^3 was processed during radioactive tests. Two levels of evaporator output value were tested: 180 dm^3/hour of concentrate (the amount of 5 drums produced) and 200 dm^3/hour of concentrate (13 drums). The average content of water in bitumen product specimen was 0.75 % (w.) - values in the range from 0.3 to 1.05 % (w.) The average salt content in stabilized regime was 40.3 % (w.), the conductivity of condensate: 0.052 mS/cm, the content of oils: 5 mg/dm^3.

3.2.2 Bituminization of resins and sludge

Objectives of complex active tests for resins and sludge batch bituminization:
Operational test of:

1. Spent resins and sludge reception from AB,
2. Suspension properties modification
3. Transport water division
4. Fugate and distillate cleaning
5. Drying of separated spent resin and sludge
6. Resins-polyethylene-bitumen mixture homogenization

Criterions of successful complex test:

1. Repumping of specified amount of resins and sludge from AB to FTC tank
2. Suspension characteristics modification, decantation in suspension tank (content of resins and sludge in suspension in the range 2-7 % W.)
3. Dosing of suspension to decanter, flushing of dosing line, automatic decanter operation
4. Sufficient output of EVH filter, less than 0,1 % particles in fugate
5. Water content in dried resins less than 5 % (W.)
6. Resins and sludge content in bitumen product more than 40 % W.
7. Water content in bitumen product less than 1 % W.

6 decantation processes were carried out in the course of radioactive tests of resin bituminization, the content of resins was in the range from 6.9 to 3.2 % w. and the treated volume of suspension was about 15 m^3. The amount of near 500 kg dry resins was embedded to bitumen matrix, 9 drums were produced. The content of water was in the range from 0.5 to 0.6 % w. and the content of resins in bitumen product was from 39 to 43 % w.

3.2.3 Over-concentration

Objectives of complex active tests for recirculation evaporator:
Test of concentrate repumping, preheating of evaporator, start-up of evaporator operation, production of overconcentrate and pumping of overconcentrate at 40 °C.

Criterions of successful complex test:

1. Correct sequential functionality of repumping and preheating systems
2. Achievement of prescribed overconcentration in automatic regime (injection rate, product flow-rate, salt content in overconcentrate and conductivity of condensate)
3. Pumping and preparedness of overconcentrate for cementation process

Parameter	Prescribed value	Achieved value
Injection rate	380 kg/h	408 dm3/h (at 80 °C)
Product flow rate	180 kg/h	202,5 kg/h
Condensate production rate	200 kg/h	247 kg/h, (at 40 °C)
Conductivity	Less than 800 µS/cm	15-35 µS/cm

The storage of prepared overconcentrate is a difficult task, so the strategy have to be the treatment of certain amount of concentrate to achieve the over-concentrate production rate equal to its consumption in the process of cement grout preparation i.e. 1 FRC/8 hours. The dosed amount of concentrate was $410dm^3$/hour with salt content $161g/dm^3$ and at these conditions the over-concentration to value $410g/dm^3$ was achieved at temperature 102°C when the rate of over-concentrate production was $157dm^3$/hour. The amount of $9m^3$ concentrate was treated during radioactive tests and 3.5 m^3 of over-concentrate was prepared.
The quality of distillate was monitored by continual conductivity measurement. The conductivity of condensed distillate during radioactive tests was in the range from 15 to 35 μS/cm. The value depended on actual heating regime, the higher value responds to intensive boiling process.

3.2.4 Cementation

Objectives of complex active tests for cementation line:

1. Dosing ability of equipment for blended zeolite cement, lime hydrate and overconcentrate
2. Cement grout mixer performance
3. Cement grout dosing to FRC container
4. Equipment flush-out
5. Tightening of filled FRC container, expedition preparation (sealing)

Criterions of successful complex test:

1. Cement grout preparation according approved receipt
2. Process control systems performance
3. Minimum mass of cement grout per batch: 800 kg ± 18 kg
4. Volume control criterion: volume per batch: 500 dm3 ± 65 dm3
5. FRC filling procedure without failure
6. Flush-out system without failure
7. Satisfactory cement product parameters achievement

The over-concentrate is mixed with lime hydrate and zeolite type of cement during cement grout preparation. The treatment prescription was tested preliminary in laboratory conditions with radioactive samples of over-concentrate. The water cement ratio 1 and stechiometric coefficient 1,1 were used during the radioactive tests.
9 batches of cement grout were prepared during radioactive tests (the free volume of 3 FRC containers). The following parameters of cement product were reached: volume weight from 1.59 to 1.70 kg/dm^3, grout outlet rate 4.2-5 s, solidification time from 45 to 72 hours, strength of test elements after 28 days 8-14 MPa (average value is 11.9 MPa) and the cement specimen leach-ability index evaluated on ^{137}Cs basis was higher then 8.

3.3 Commentary to trial operation preparation works.

Before the completion of active complex test there was an assumption that the FTC will be set into active trial operation without a larger timing relationship. Later it was proved that this assumption was not right because of many reasons (the request for the technology completing,

for completing the measuring accuracy equipment, the long process of approval) it came to the long delay.
The license for the active trial operation was finally certified on 8 October 2007. After the license was certified the advance working for the initiation of technology FTC into the trial operation have started.
First the technology of bituminization of radioactive concentrate has being prepared. We assume that the first bituminization will start in the middle of November 2007, during which time we plan to process 30m^3 of radioactive concentrate from NPP EMO.
After finishing the bituminization of radioactive concentrate, we would like to process approx. 500kg dried radioactive resins by the end of the year 2007 and to start up the cementation so we could fill 10 pieces of FRC.

4. Evaluation of experience gained

Interdependences within process parameters and treatment product properties

The interdependences between individually monitored technological process parameters and the values of characteristic product parameters can be defined on the basis of measured values and general operational experiences. **Table No. 1** summarizes the key parameters of individual technological procedures with essential influence to performance and the achievement of prescribed monitored product parameters.

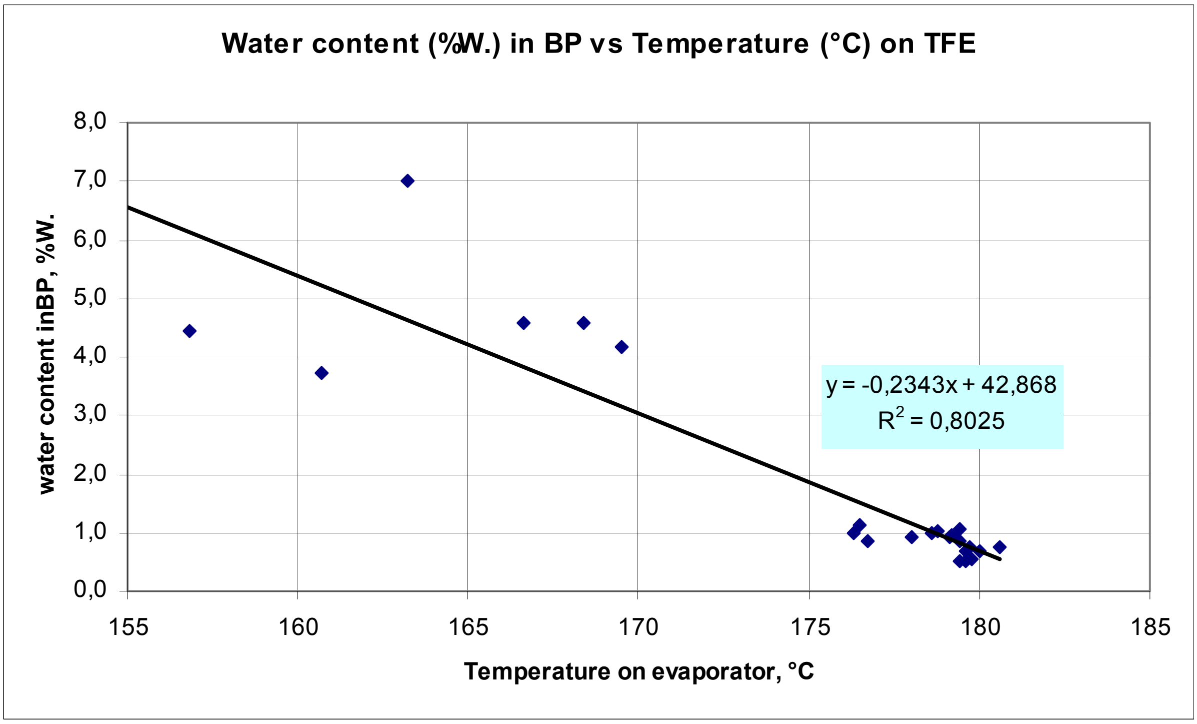
Table No 1: Key parameters of technological processes

Process	**Key parameters**
Bituminization on TFE	Heating steam temperature/ pressure Value of under-pressure in area of bitumen product outlet Temperature of injected concentrate Temperature of dosed bitumen Speed of TFE rotor
Batch bituminization	Content of sludge in resin-sludge mixture Temperature of heating steam in drier Water content in dried suspension Water tightness of drier’s sealing valve Polyethylene content in melted bitumen
Overconcentration	Temperature of heating steam Temperature in evaporator Conductivity of distillate in separator Salt content in specimen
Cementation	Weight measuring accuracy for all components Salt content in overconcentrate Temperature of overconcentrate The dosing order of components Time duration of mixing phases Water-cement ratio Lime-overconcentrate ratio

4.1 Water content

The water content in bitumen product is an important product parameter. The dependence of water content in bitumen product on TFE working temperature value is obvious from data displayed on **Pic. No 1**.

Pic. No 1: Water content in bitumen product vs temperature on TFE



4.2 Decanter operation

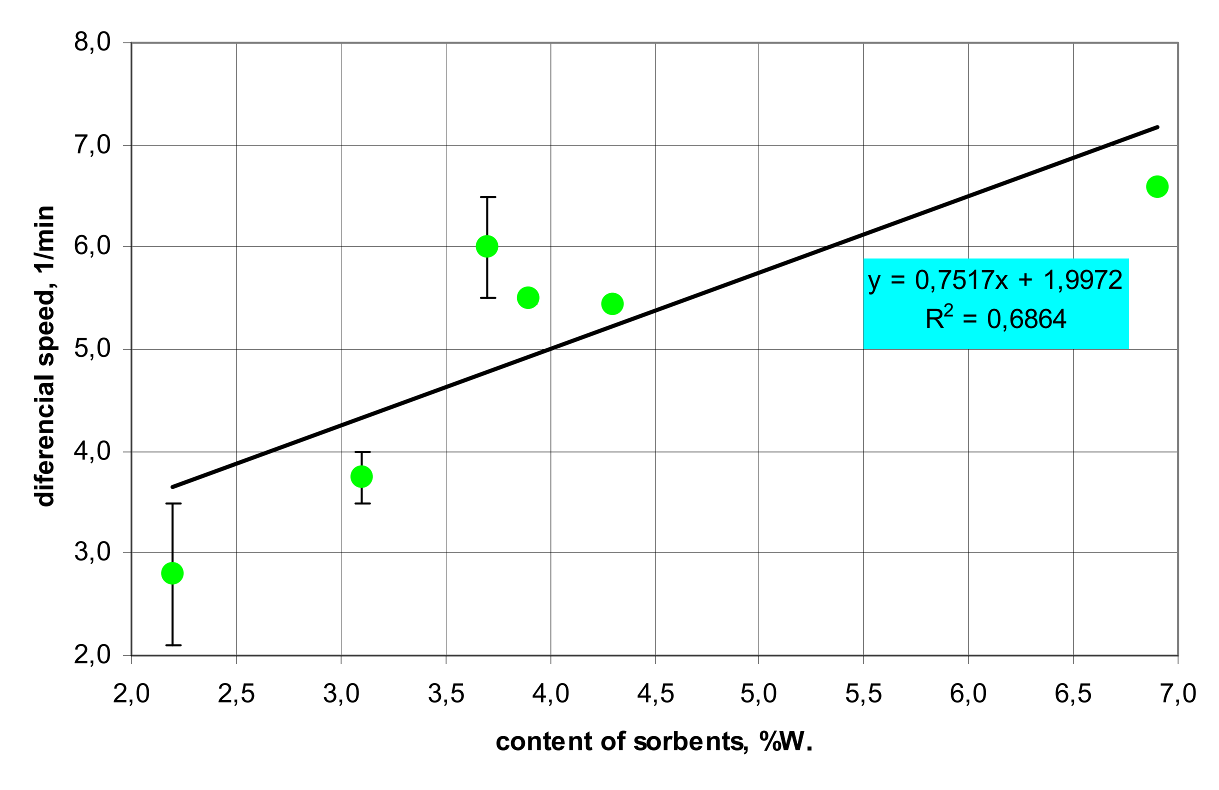
The value of differential rotation speed on decanter's lifting screw has to be chosen with effect on torque between value 1 and 1.4. This value ensures the transport of needed dry residue amount of decanted material.

This differential rotation speed has to be adjusted properly when the ratio between resins and sludge is variable. The dependence of transported resins-sludge mixture amount on decanter's lifting screw differential rotation speed is displayed on **Pic. No 2**

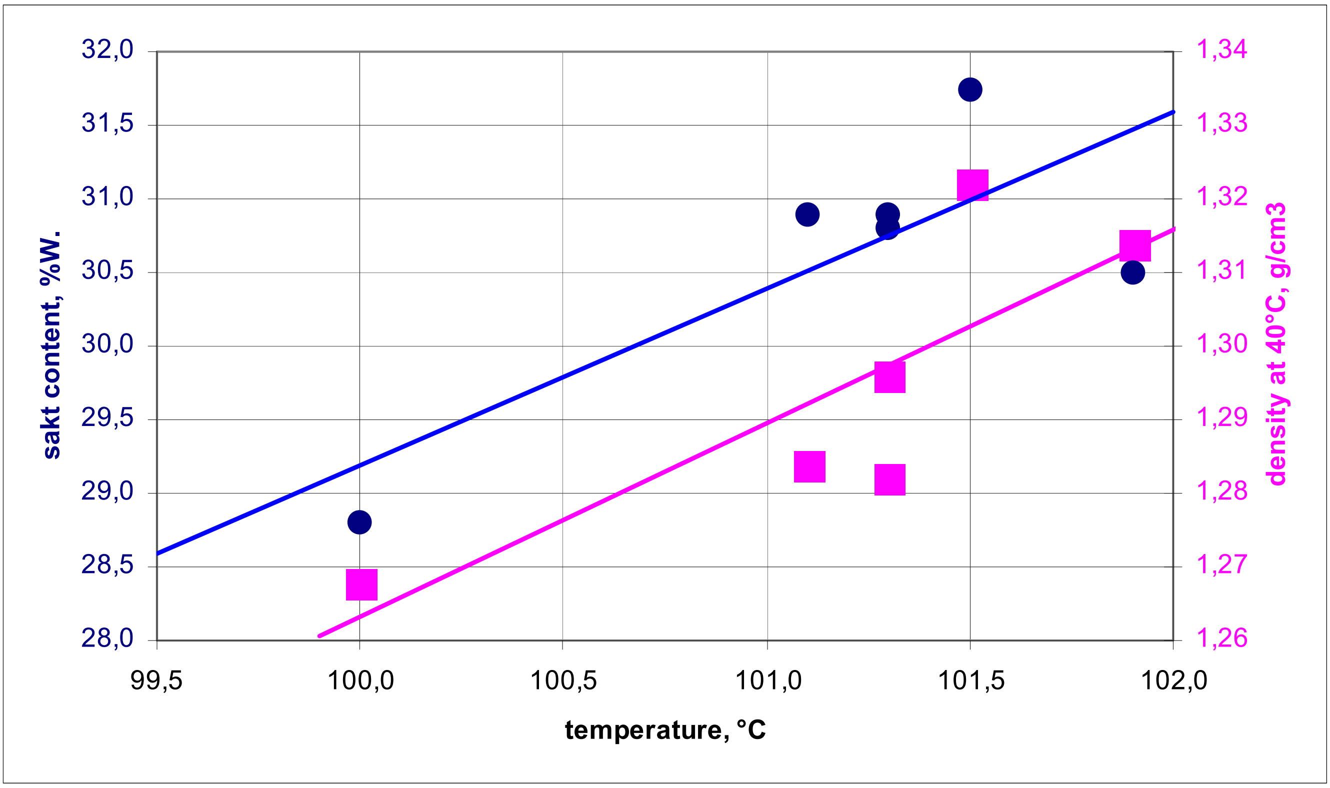
4.3 Boiling point dependence for overconcentrate

The dependence of over-concentrate's boiling point on salt content value is utilized in the process of re-circulating evaporator operation control. So, for example, for the required overconcentration to value of salt content 30-33 % (W.) is the boiling temperature of 101,5-101,9 °C designated. The dependence of over-concentrate's density and the salt content in over-concentrate on evaporators working temperature is given on **Pic. No 3**

Pic. No 2: Decanter's differential speed vs resins-sludge mixture content in input suspension

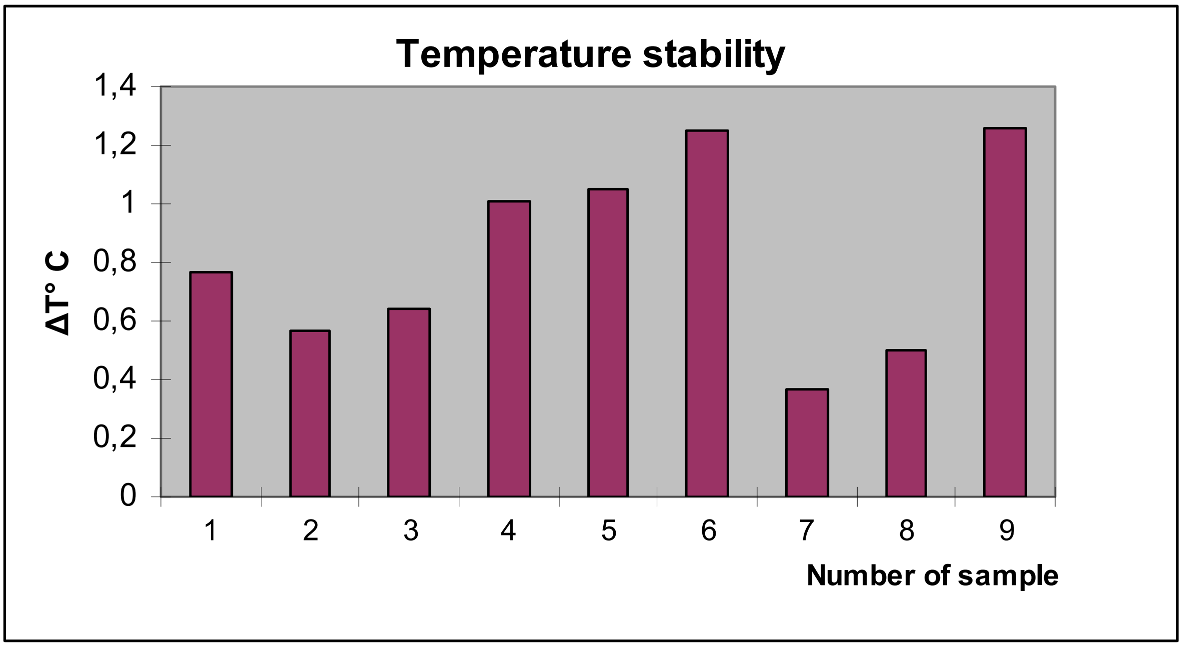


Pic. No 3: Salt content in overconcentrate vs temperature in separator



4.4 Thermal stability

The thermal stability of bitumen product samples is regularly monitored in the temperature range from 50 to 250°C**.** The reason is safety relative and there is an effort to lower the risk of possible exothermic reaction development.
The results of thermal stability determination for bitumen product samples are given on Pic. No 4. The allowed limit of temperature difference is ΔT < 10 ° C. Above the limited difference the risk of oxidation-reduction reaction is possible.
As it is visible on this picture, the samples of bituminized product show sufficient thermal stability in range of temperatures 50 – 250 ° C.



5. CONCLUSION

The description of technological equipment, technological procedures and the description of final product preparation suitable for final disposal in the frame of Final Treatment Centre Mochovce are given
The experience gained during model and radioactive testing procedures is analyzed and commented.
The phase of trial operation preparation is described from the point of view the specific actual conditions.
The description of mutual influences of individual key technological parameters is displayed.
The fulfillment of the projected output and qualitative parameters defined in criterions of successful test results for all technological facilities are displayed.