HEAVY WATER PRODUCTION IN ROMANIA: TWILIGHT OF AN INDUSTRY & DAWN OF NEW PERSPECTIVES

PRODUCŢIA DE APĂ GREA ÎN ROMÂNIA: DECLINUL UNEI INDUSTRII & DEBUTUL UNOR NOI ORIZONTURI

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Abstract: *In November 1979 it was issued the Decree for the establishment of the Heavy Water Plant at Drobeta Turnu Severin. Growing as part of an ambitious nuclear program, this chemical production unit delivered the first heavy water batch in 1988 and it was recognized as the only heavy water producer in Europe and the largest in the world. In 2013, based on Government Decision no. 85/2013, the Heavy Water Plant entered in insolvency, and 3 years later was declared bankruptcy.*

A historical review of the manufacturing of the inventory for the first filling and subsequent make-ups for NPP Cernavodă Units 1&2 and, also, of the estimated inventory for future potential NPP Cernavodă Units 3&4 is delivered with highlights of achievements, drawbacks and challenges encountered within this industrial saga.

This paper aims to filter technical, economical and political aspects that could act as decision fundaments for future plans for heavy water stocks management (including the tritiated ones) or actions for redrawing the heavy water and tritium R&D program in Romania and for the prospection of new industrial developments.

Keywords: heavy water, tritium, management, resource

Rezumat: *În noiembrie 1979 a fost publicat Decretul de înfiinţare al Combinatului Chimic pentru producerea apei grele Drobeta Turnu Severin.*

Dezvoltându-se ca parte a unui program nuclear ambiţios, această unitate de producţie chimică a livrat prima şarjă de apă grea în 1988 şi a fost recunoscută drept singurul producător de apă grea din Europa şi cel mai mare din lume. În 2013, în baza Hotărârii Guvernului nr. 85/2013, uzina de apă grea intră în insolvenţă, iar 3 ani mai târziu este declarat falimentul.

Este prezentat un istoric al fabricaţiei inventarului de apă grea necesar pentru primă umplere şi completare ulterioară pentru unităţile 1 şi 2 de la CNE Cernavodă şi, de asemenea, un istoric pentru inventarul estimat ca necesar pentru viitoarele unităţi 3 şi 4 ale CNE Cernavodă; sunt subliniate aspecte importante referitoare la realizările,

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dar şi privind dificultăţile și provocările care au trebuit să fie înfruntate în această adevărată saga industrială.

Această lucrare își propune să scoată în evidenţă aspecte tehnice, economice și politice care ar putea să fundamenteze deciziile referitoare la planurile viitoare de gestionare a stocurilor de apă grea (inclusiv cele tritiate) sau acțiunile în vederea revizuirii programului de cercetare - dezvoltare în domeniul apei grele și tritiului în România și pentru prospectarea unor noi direcţii de dezvoltare industrială.

Cuvinte cheie: apă grea, tritiu, management, resursă

1. Introduction

Heavy Water Plant (RAAN ROMAG PROD) was founded in 1979 and formerly was known as Drobeta Turnu Severin Chemical Plant. Its development was an exclusively Romanian achievement (research, design, execution, commissioning and operation) and this unit was an unique top technology facility of the Romanian industry.

In the `80s this unit was part of an ambitious nuclear program designated to sustain the economic development of the country and its energy independence. This goal was possible because ***the human & financial resources needed*** for this ***were available and allocated*** and, also, ***at that time the project had a strong political support and involvement***.

The first production line was tested starting with September 1987, and the first drop of heavy water was produced in July 1988. On July 17, 1988, heavy industrial water was obtained at ROMAG PROD - Drobeta Turnu Severin, at parameters set for nuclear reactors type CANDU 6 (table 1). At the beginning, in the first years after commissioning, the unit was shutdown for about three years (between 1990 – 1992) to upgrade technological equipment and environmental surveillance and protection systems. The modernization process had as result the improvement of the plant feasibility and had shortened the manufacturing time for a new supply of heavy water. During years this unit was recognized as the only heavy water manufacturer in Europe and the largest in the world.

2. Case study

Table 1. RAAN ROMAG PROD – heavy water parameters (source: RAAN ROMAG PROD website)

Heavy Water Quality As per Technical Sheet (that met AECL requirement for CANDU type reactors – Technical Specification TS-XX-38000-001, AECL, 01.02.1999)		
Parameter	**Value**	**Unit**
Isotopic concentration	Min. 99.78	% wt. D_2O
Conductivity	Max. 5	μS/cm
Turbidity	Max. 1	NTU (ppm SiO_2)
Organics ($KMnO_4$ demand)	Max. 10	mg/kg
Chloride	Max. 0.5	ppm
Tritium	none	μCi/kg
NOTE: 1. Also, could be delivered one grade of heavy water with concentration greater than 99.96 D_2O and four grades of depleted low-weight water with concentration ranging between 0 and 80 ppm D_2O. These grades are patented and homologated. 2. Considering high heavy water quality, ROMAG PROD is recognized on European and Asian markets, being exporter of nuclear grade heavy water supplies in South Korea, China, Germany, etc.		

The plant is situated on the territory of Rascovesti village, Izvoru Bârzii parish, at a distance of about 7km from Drobeta-Turnu Severin (Figure 1), and the area occupied by the plant is estimated at approximately 82 ha.

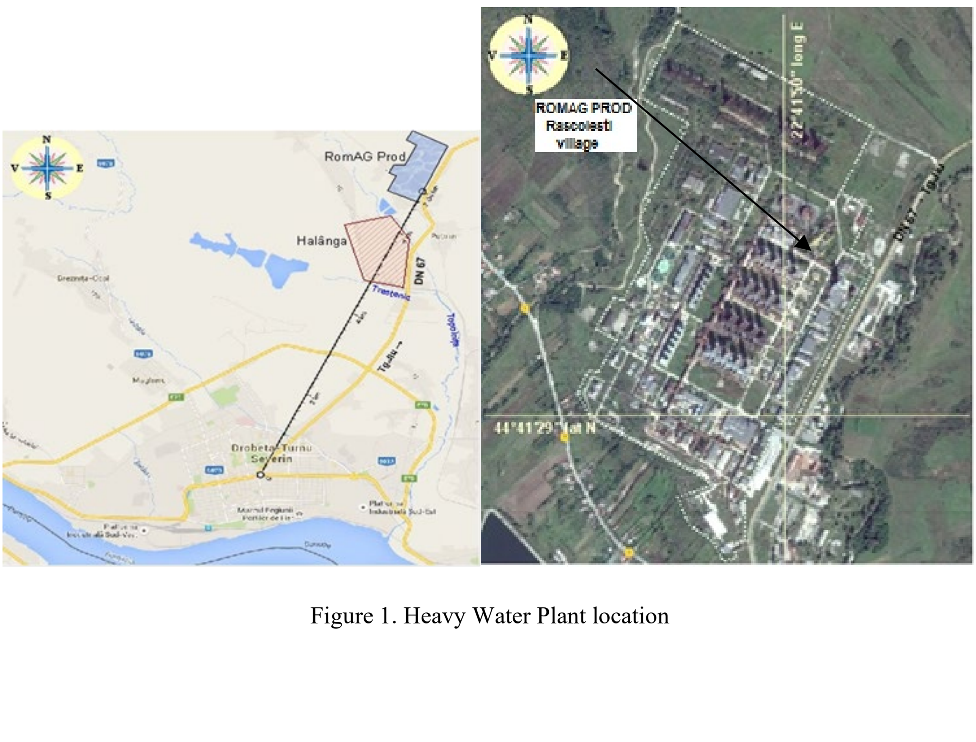

Figure 1. Heavy Water Plant location

Of the four production lines related to the first stage of development of the Water Factory, only three (GS1, GS3 and GS4) were put into operation. The process equipment from ROMAG PROD is made from rolled and forged G52/28 steel grade material developed in the eighties at Steel Plant Galati based on National Technical Normative NTR 440/83. It was clearly a particular attention to be paid to the materials from which the biterm separator (columns and pipes) were built. Wet sulfide hydrogen and water solutions with hydrogen sulfide (pH ~ 3) are very corrosive agents. For competitiveness, this carbon steel grade, developed in Romania was characterized by a smooth, homogeneous microstructure, it was subjected to a stress relief treatment and 100 % inspected in fabrication. The corrosion resistance was provided by a thermo-chemical treatment of the exposed surfaces, called "pyrite layer controlled formation".

This material was fully characterized in order to establish it fitness for use in hydrogen bearing environments as structural steel for isotopic exchange columns walls. Due to long term action of mechanical and thermal stresses in the presence of an extremely active and aggressive service environment (e.g. H_2S aqueous solutions) during service life of this plant an extensive RD program was developed to guarantee industrial safety. This preoccupation resulted in methodologies of action for long term serviceability of the equipment and other technological components at RAAN ROMAG PROD, in-situ experimental programs for the evaluation of long term behavior of steels that are serviced in hydrogen bearing environments, particularly for fine grained C-Mn steels serviced in H_2S environments etc.; methodologies to evaluate the technical state of pressure vessels for & after the extension of service life and the repair program for the isotopic exchange columns were developed and agreed with the Romanian regulatory body for pressure vessels (ISCIR).

This exceptionally complex program (and unique technical solution) was settled with the support of Romanian specialists and technicians considering that the following items are important for the development of repairs and monitoring schedule:

- The type of equipment to be evaluated;
- Technical expertise;
- Available resources.

As part of the activities it was demonstrated that it is possible to recover the capability of ROMAG equipments by repairs performed on metallic structure (deposition of metallic layers by welding in those areas reported as non-conformity areas (erosion – corrosion cavities)).

The heavy water process is based on the isotopic exchange of process water and hydrogen sulfide in a biterm system in GS (Girdler-Sulphide) plants – figure 2, where a primary deuterium oxide concentration of about 5-7 %.

The reaction occurs in the liquid phase, between process water and dissolved hydrogen sulfide, on special sieve-type plates:

$$D_2O + H_2S \underset{30^0 C}{\overset{130^0 C}{\rightleftarrows}} H_2 0 + D_2S \quad (1)$$

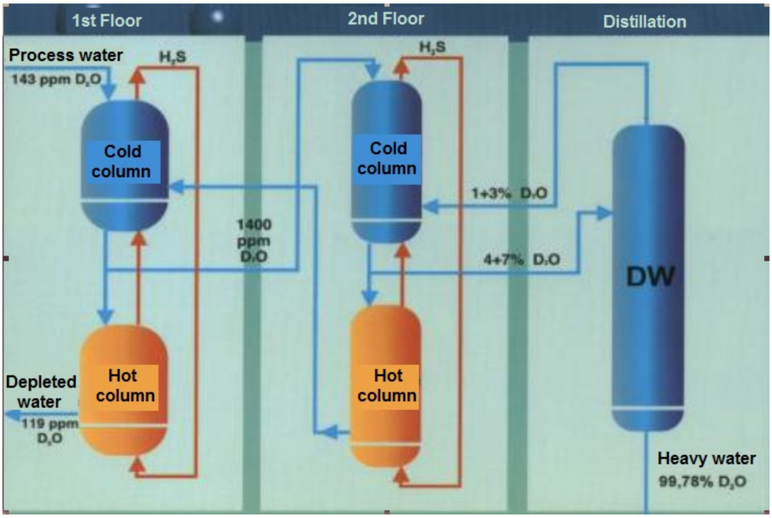

Figure 2. Heavy Water manufacturing process (source: RAAN ROMAG PROD website)

The basic element of the Girdler-Sulphide process is the pair of liquid-gas contact columns, of which the cold column works at temperatures of 30-35 ºC and the hot column at 110-130 ºC. Process water, with a deuterium content of about 143 ppm, flows from top to bottom through the cold and then the hot column, in counterflow with the hydrogen sulfide conveyed by a compressor on the base of the hot column. Water is progressively enriched in deuterium as it flows through the cold column and it is progressively depleted in deuterium while flowing through the hot column. The effluent leaving the hot column contains about 120 ppm deuterium. Thus, by deuterium enriching on each tray the heavy water concentration reaches about 1400 ppm. The production of the first floor is even greater as the deuterium concentration of the effluent is lower. On the second floor, the water resulting from the A, B and C biterms of the first floor is concentrated from 1400 ppm to 5-7% D_2O. The enriched water from the second floor feeds the vacuum distillation plant, DW.

The main dynamic equipment was the hydrogen sulfide recirculation compressor, virtually the vital element of the process, of high design complexity and therefore very expensive, so the plant was equipped with only active equipment. Due to the corrosive action of wet hydrogen sulfide, the compressor was made from special stainless steel.

The final concentration, up to a minimum of 99.85%, was achieved in the vacuum distillation plant, where it is obtained the finished product - heavy water with parameters required for a CANDU reactor, according to the quality grade imposed by Cernavoda NPP.

For heavy water quantities produced by ROMAG PROD installations were taken a number of measures to ensure the long term preservation (qualitative and quantitative). The heavy water inventory was stored under inert gas in 220 liter steel cylinders and in tanks of 50 m^3, in safe warehouses.

During 1994 – 1998, this plant produced heavy water inventory with quality parameters requested for Unit 1 at Cernavodă NPP (556 t). During 1999-2004 was produced necessary heavy water inventory for first load for Unit 2 from CNE Cernavodă.

Several quantities were exported, in compliance with the Romanian legislation in force, to other countries such as Korea, China, Germany, USA.

Currently, it was produced the whole quantity set by law for the operation and extension of service life in case of four CANDU units at Cernavodă NPP (first fill & make up heavy water).

And, therefore, heavy water production has been stopped since 2015; previously in 2013, Heavy Water Plant entered in insolvency and 3 years later was declared bankruptcy.

For this reason, installations are in different stages of conservation, and the only activities aimed for the management of the existing heavy water inventory are carried out based on former RAAN ROMAG PROD procedures.

The situation is frozen in accordance with the initial design. The unit was designed with two development stages:

- Stage I - consisting in four isotopic exchange modules GS1, GS2, GS3 and GS4; this stage has been partially commissioned and produced the inventory forecasted for the development of the Romanian nuclear program;
- Stage II - consisting in three isotopic exchange modules GS5, GS6 and GS7; this was never commissioned and the construction was stopped in 2004.

3. Conclusions

Due to insolvency, and lately to bankruptcy, the resources for the management of heavy water inventories were a great challenge for the entity and for technicians. For this reason, the Government initiated discussions with all involved parties in order to find the best solution for heavy water inventories preservation.

Starting with 2017 a new entity was created in order to preserve the national reserve of heavy water. But this is not the end of the epic. Due to the evolution in the years before insolvency and further, the separation of another entity from the dying Heavy Water Plant is a delicate and hard topic.

In fact this new entity will have to re-design its structure and skills and capabilities, on the remains of the Heavy Water Plant. A lot of modifications and reallocations are to be imagined in order to guarantee de serviceability of this new entity and, also, to meet the requirements stated by law for the preservation of the national heavy water inventory.

In the beginning of the paper we mentioned that for the development of this unique heavy water plant in Europe both legal, economical and technical aspects were correlated. Now the same approach should be considered.

The social problem, the human resource (old staff, retirements, no new skilled young personnel trained for operation of the installation), lack of financial resources, or insufficient & delayed budgets, hesitations in the decisional process could impair the planning of the future steps for the transition to this new management entity for the existent virgin heavy water inventory. For this reason a strong governmental support is needed, sustained by the voices of recognized specialists that were the ones that in the past dedicated all their knowledge and efforts for the Drobeta Turnu Severin Chemical Plant.

R E F E R E N C E S

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