HEAT STORAGE AND TRANSFORMATION

Paper presented at the ZAE-Symposium 2001, 'Heat and Cold Storage' Munich, 3-5 October 2001

P.W. Bach
W.G. Haije

Revisions			
A	October 2001; Final version		
B			
Made by:	Approved by:	Issued by:	ECN Energy Efficiency in Industry
P.W. Bach W.G. Haije	P.W. Bach	P.T. Alderliesten	

Abstract

In order to increase the energy density of a thermal storage unit for domestic use, experiments have been performed with two different PCM types: a salt hydrate and a paraffin. The paraffin shows the best performance, with a useful thermal storage density of more than 2 times that of water.

The development of the SWEAT (Salt-Water Energy Accumulation and Transformation) system is directed to cooling applications (5-15°C) in industry and in commercial buildings using waste heat or heat from co-generation at about 80°C. The main focus is on solving the corrosion problem. Therefore a number of polymer coatings were tested under SWEAT conditions and only one combination of epoxy resin with hardener appeared to be applicable. Cycling experiments are currently performed to test the long-term behaviour of the coating under realistic conditions.

Current research on the high temperature heat transformer for steam generation in industry is focussed on the determination of the thermodynamic and kinetic properties of the working pairs, as well as the heat conductivity. A simulation model in Matlab/Simulink has been developed in order to explore the behaviour and performance as a function of the system layout.

CONTENTS

1. INTRODUCTION

Dutch national policy aims at a 33% energy saving by the year 2020. About 80% of the total energy production is related to heat demand. Improving the thermal energy efficiency with heat storage and transformation, is therefore an obvious target for R&D.

Heat storage is necessary in order to accommodate differences in time between heat production and heat demand, which is gaining importance with the installation of decentralised power generation (co-generation, intermittent solar thermal energy, heat pumps) and batch-wise production in industry.

Suitable storage media are, besides water for sensible heat storage, phase change materials and materials, that allow for dissociation/recombination reactions, for example salt hydrates. These reactions offer, in addition, also the possibility to transform the stored energy either to higher or lower temperatures for heating or cooling purposes.

1.1   Heat storage in PCM

In order to increase the energy density of a storage unit for domestic use and to improve the power performance with a constant temperature at (un)loading, the application of phase change materials is recommended. Experiments have been performed with two different PCM types: a salt hydrate and a paraffin.

1.2   Salt hydrate PCM

The inorganic PCM tested, is an experimental batch of Cristopia PCM S-64: a sodium hydroxide-monohydrate with a melting temperature of about 64°C and a heat content of 56 kWh/m^3 at a ΔT of 6°C. The salt hydrate is packed in a spherical PE-nodule with a diameter of 77 mm. A test system, consisting of a 0,350 m^3 storage tank and a 40 kW heating and cooling system with water circulation for heat transfer, has been filled with about 700 PCM nodules, see Figure 1.1.

Figure 1.1 *Heat storage test tank filled with PCM nodules*

According to the specifications of commercially available Cristopia PCM nodules for cold storage a supercooling of about 2°C should be expected. After tests with some individual PCM S-64 nodules, however, degradation of the heat storage behaviour is measured: an increase in the supercooling temperature from less than 5°C to more than 10°C after 3 cycles.

Also in the test tank the discharge temperature has to be decreased far below the melting temperature, in order to discharge the nodules(see Figure 1.2.) It is observed that after some 100 cycles about 20% of the nodules releases the latent heat at supercooling of 5°C, about 30% at 9.5°C and 50% at 14°C.

The performance of this experimental batch is not acceptable for heat storage applications in dwellings. The main advantage of PCM storage, which is a high heat storage density in a small temperature range, is lost due to the large supercooling.
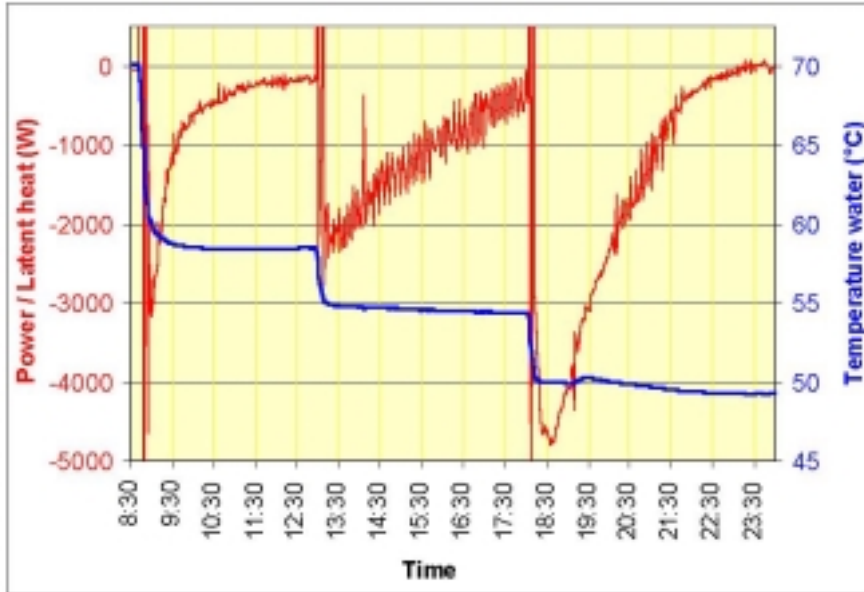
Figure 1.2 *Discharging behaviour of the PCM-S-64 nodules in the storage tank as a function of the supercooling temperature*

1.3   Paraffin PCM

Paraffin wax is an attractive material for heat storage applications. High latent heat storage capacities over a narrow temperature range can be obtained and these PCM's are ecologically harmless and non-toxic. However, melting of the material causes segregation in heating systems based on water circulation. A new development is binding the paraffin in a cross-linked sponge-like structure. This ensures that the PCM does not leak out of the supporting structures, even when in the liquid state. This material PK RT 50, which is under development at Rubitherm, contains approximately 80% RT 50 paraffin with a melt enthalpy of 195 kJ/kg and a melting point close to 54°C. The grain-like structure offers the possibility for intensive heat transfer by a water flow.

Melting and congealing experiments have been performed in a 0,3 l glass container (see Figure 1.3).

Figure 1.3 *Test container and the porous structure of the paraffin grains*

The wax grains melt and congeal according to the specifications and the useful thermal storage density in the 45-55°C range is more than 2 times that of water. See Figure 1.4. However, some sticking and compacting of the wax grains of this experimental batch has occurred, which can have influence on the water flow in a larger container (see also Figure 1.3).
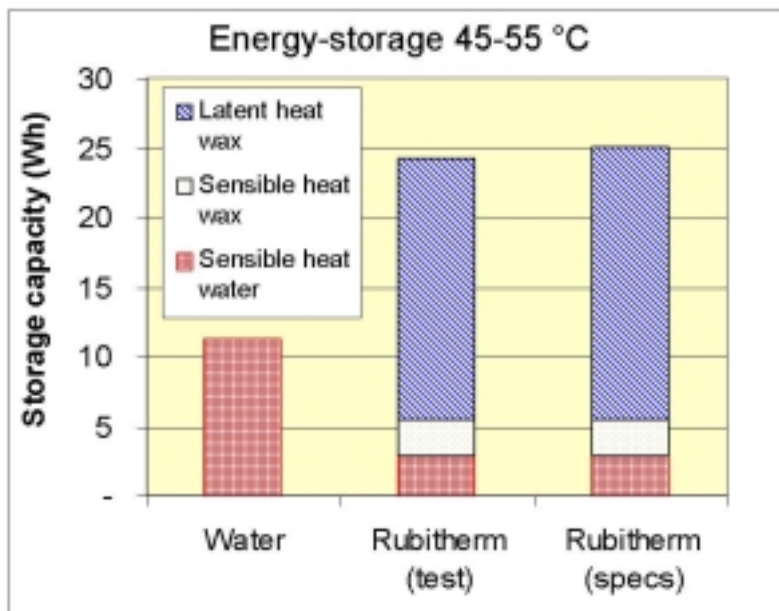

Figure 1.4 *Heat storage capacity in the 0.3 l glass container*

The PK RT50 material shows a very stable phase change behaviour over more than 70 temperature cycles. The profile of the power curve in Figure 1.5 shows a hysteresis effect of about 2.5°C. The two maxima are indicative of a bimodal chain length distribution of the RT 50 paraffin and its width.
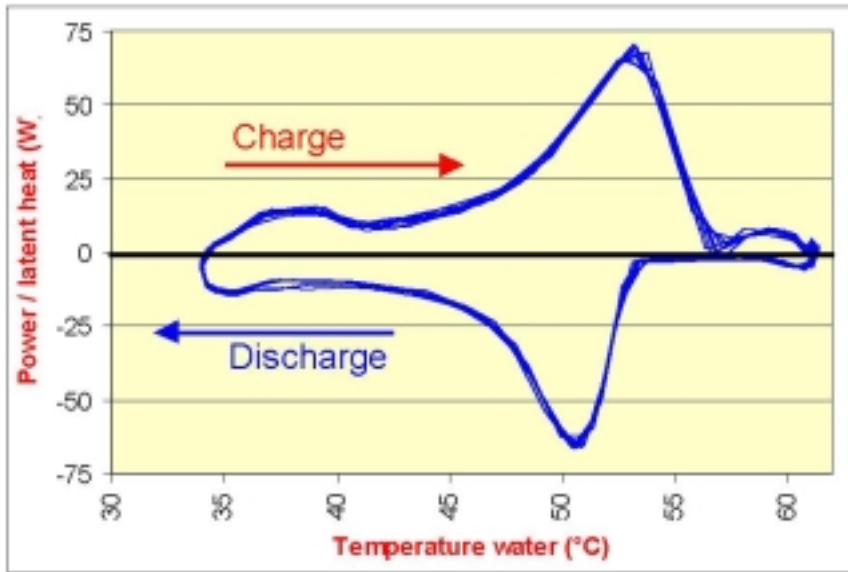
Figure 1.5 *Latent heat power curves of Rubitherm PK RT 50 in water. Heating and cooling rate 0.5°C/min*

2. SOLID-VAPOUR ABSORPTION: HEAT STORAGE AND TRANSFORMATION

2.1 Solid-vapour absorption cooling: SWEAT development

The SWEAT (Salt-Water Energy Accumulation and Transformation) system is based on the reversible hydration of Na_2S:

$$Na_2S \cdot 0,5H_2O + 4,5 H_2O \leftrightarrow Na_2S \cdot 5H_2O + Heat \ (\Delta H_{reaction}= 3,9 \ kJ/g)$$
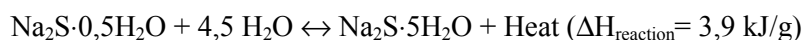
A typical SWEAT unit consists of two vessels connected with a pipe. One , the accumulator, contains the sodium sulphide hydrate, the other, the evaporator/condenser, water. When (waste)heat is supplied to the penta-hydrate at about 80^oC it decomposes in the lower hydrate and water vapour. The vapour condenses in the condenser and the heat of condensation is released to the ambient. When the reaction is completed the system is charged.

Separating the two vessels by a valve results in heat or cold infinite storage with virtually no loss: only 15% in the form of sensible heat.

Discharging the system is accomplished by following the reverse process. Heat from the ambient is used to evaporate water and thus causes a cooling effect to 5-15°C. The heat of reaction in the accumulator is released to the ambient.

The system is to be used for cooling in industry and the built environment.

The main problems encountered during the development of this system concerned the corrosion reactions of the salt with the heat exchanger in the accumulator and the existence of a second phase, $Na_2S \cdot 2H_2O$. The first led to H_2 production and thereby blocking of the condenser, the second to a larger ΔT necessary for charging.

Corrosion research was focussed on coating the wire fin heat exchanger with an inert material. The degree of coverage should be 100,00%, this also implies 0,00%porosity. Materials considered were supposedly inert metals like Ni, Au and Pt, ceramics and polymers. It turned out that *no* metal is inert in a Na_2S-H_2O environment. Ceramics are of no use due to the difference in thermal expansion as compared to copper used for the heat exchanger.
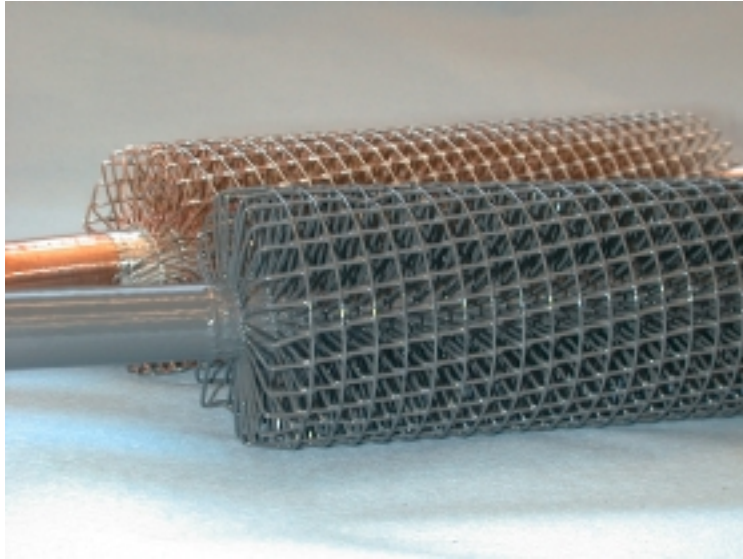
Figure 2.1 *Bare and epoxy coated wire-finned heat exchanger*

A number of polymer coatings were tested under SWEAT conditions and only one combination of epoxy resin with hardener appeared to be applicable. The main technique for quality control has been electrochemical impedance spectroscopy.

The second difficulty was to find a way to apply this coating onto the heat exchanger without defects. Powder spraying on a carefully prepared heat exchanger surface ultimately yielded the required initial conditions: no defects (Figure 2.1). To this end a dedicated electrochemical characterisation method has been devised.

Cycling experiments are currently performed to test the long-term behaviour of the coating under realistic conditions (Figure 2.2).
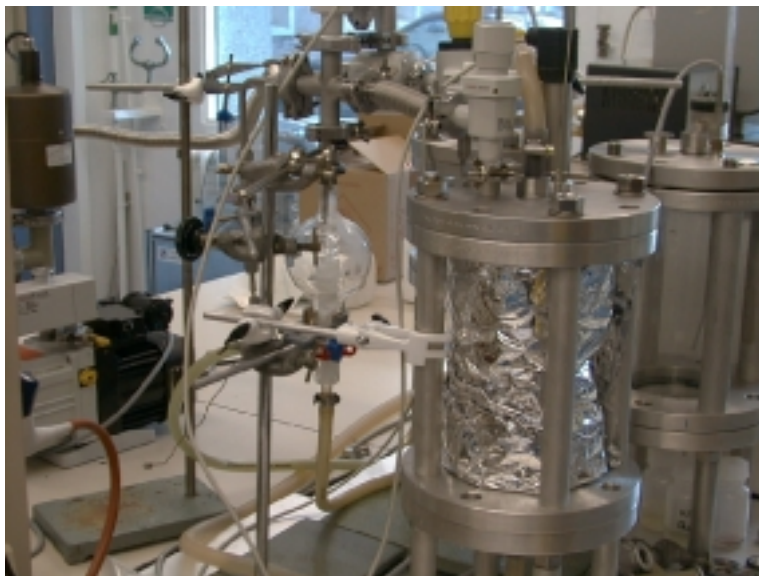

Figure 2.2 *Cycling set-up: on the left the glass evaporator/condenser bulb, on the right the accumulator wrapped in insulating foil*

When these experiments have a positive result i.e. an expected life-time longer than 5 years, a 10 kW prototype system for continuous process cooling will be built and tested in an industrial environment.

In order to have numerical information on the operation of a SWEAT system as a function of geometry, heat exchanger configuration, heat conduction enhancing additives, etc., a computer model has been developed using the package Matlab/Simulink. In Figure 2.3 simulation results of a charging and discharging run are depicted. The red curve represents the power absorbed or released by the accumulator, the blue one the same for the evaporator/condenser. The result is calculated for a SWEAT pre-prototype unit consisting of six metres of wire-finned heat exchanger containing 2,65 kg of dry Na_2S. On average this leads to a cooling power density of about 0,6 kW/kg dry Na_2S.
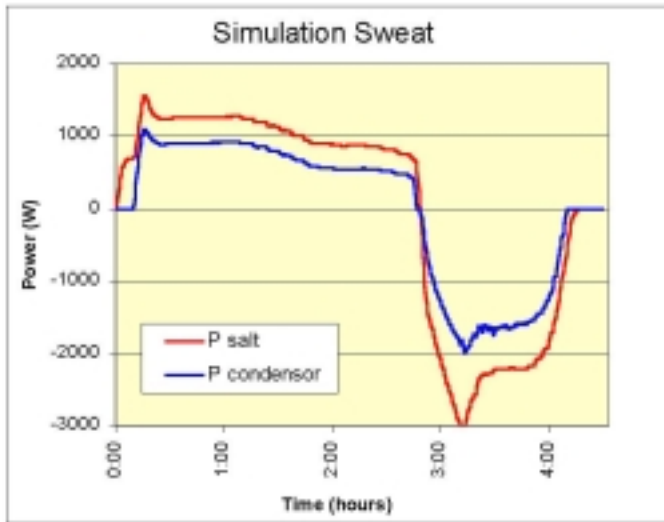
Figure 2.3 *Simulation results of subsequent charging (P >0) and discharging (P<0) runs of a SWEAT pre-prototype*

2.2 Solid-vapour absorption heat transformers: steam generation in industry

In the Netherlands alone about 100 PJ/a worth of industrial waste heat in the temperature range of 50 to150°C is actively cooled and dissipated into the environment (Figure 2.4). On a European scale this amounts to approximately ten times this number [1].
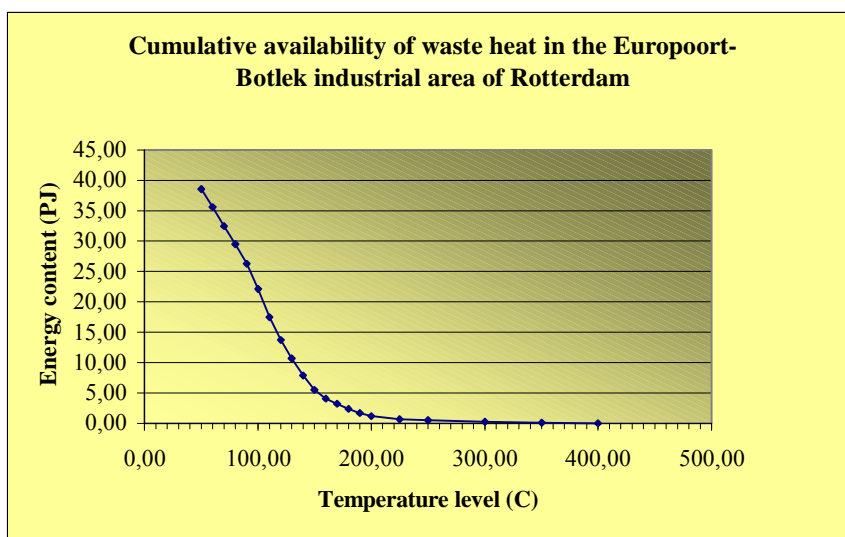
Figure 2.4 *Cumulative availability of waste heat in the Europoort-Botlek industrial area of Rotterdam*

In recent years much effort has been put into the development of gas fired or heat driven solid sorption chemical heat pumps and heat transformers [2,3,4,5], for heating as well as cooling purposes. The heat driven one especially is being a key issue for reusing industrial waste heat. The working principle of this apparatus is based on the exothermic absorption and endothermic desorption of vapour in solids, e.g. water in silica or zeolites [2,3], ammonia in metal salts [4] or ammonia in carbon [5]. The heat transformer cycle of the following two salt-ammonia equilibria is depicted in Figure 2.5:

LTZ: $\qquad$ $MnSO_4 \cdot 2NH_3 + 4NH_3 \leftrightarrow MnSO_4 \cdot 6NH_3 + Heat$

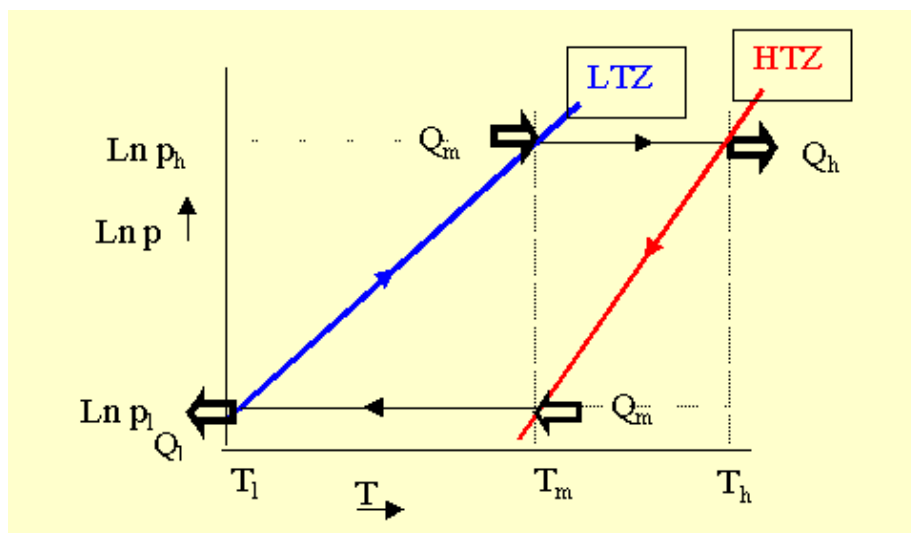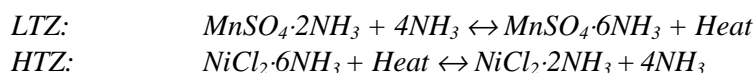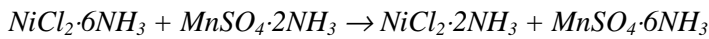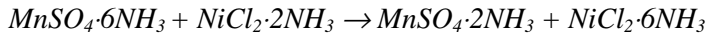HTZ: $\qquad$ $NiCl_2 \cdot 6NH_3 + Heat \leftrightarrow NiCl_2 \cdot 2NH_3 + 4NH_3$

Figure 2.5 *Thermodynamic cycle of a chemical heat transformer based on two salt-ammonia pairs. $T_l=40^oC$ (ambient), $T_m=140^oC$ (waste heat), $T_h=240^oC$ (steam)*

The thermal effects and thus the attainable energy densities are much larger, about one order of magnitude, in the case of chemisorption as is the case in e.g. ammonia-metal salts pairs, than in the case of physisorption of e.g. water in silica. As opposed to the conventional liquid/vapour absorption heat pumps or transformers there is no fundamental limit to working temperatures and much larger temperature lifts, typically 100^oC or more, can be obtained. Furthermore this kind of systems have the intrinsic property of thermal energy storage so that asynchronous demand and availability can be accommodated.

Thus it is possible to use the surplus of industrial waste heat and upgrade it with an efficiency of about 35% to utility level: e.g. the middle pressure steam net (T > 200^oC, p > 13 bar).

Current research is focussed on the determination of the thermodynamic and kinetic properties of the working pairs using a high pressure DSC, as well as the heat conductivity. An experimental set-up for heat conductivity measurements was designed and built, which allows for performing measurements on the ammoniated salts as a function of pressure, temperature, bed density, heat exchanger geometry and additives.

A simulation model in Matlab/Simulink has been developed in order to explore the behaviour and performance as a function of the system layout. Figure 2.6 shows a typical result of a simulation of the subsequent net reactions

$$MnSO_4 \cdot 6NH_3 + NiCl_2 \cdot 2NH_3 \rightarrow MnSO_4 \cdot 2NH_3 + NiCl_2 \cdot 6NH_3$$

$$NiCl_2 \cdot 6NH_3 + MnSO_4 \cdot 2NH_3 \rightarrow NiCl_2 \cdot 2NH_3 + MnSO_4 \cdot 6NH_3$$

during which the manganese sulphate bed is first heated to 140°C using waste heat and the nickel chloride bed is heated through the exothermic absorption of ammonia from 140°C to 240°C. Subsequently the two beds are cooled to 40°C and 140°C respectively during which the second reaction proceeds. If the thermal masses are not taken into account the two figures fit exactly into each other.

In about two years' time a continuous high temperature heat transformer proof-of-concept of about 5 kW will be built and tested.
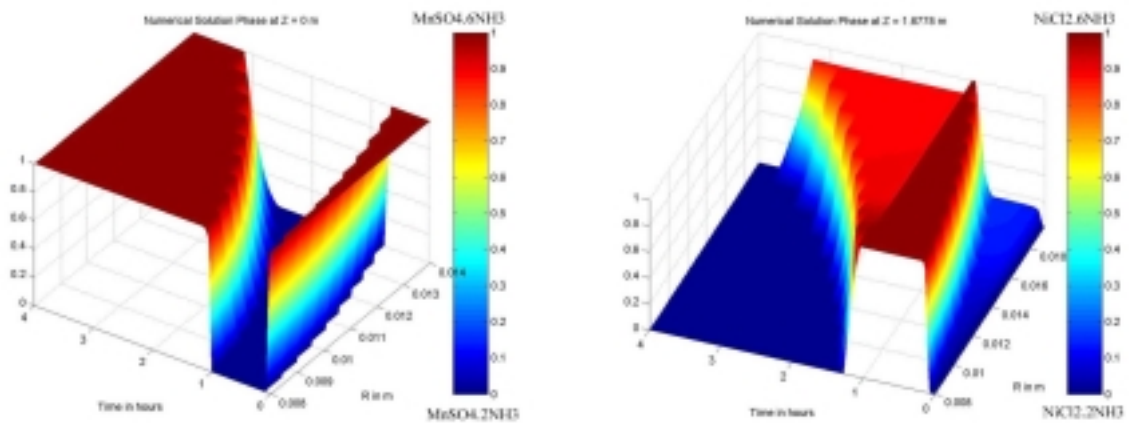

Figure 2.6 *Simulation results of simultaneous desorption of NH$_3$ from NiCl$_2 \cdot 6NH_3$ (right) and absorption in MnSO$_4 \cdot 2NH_3$ (left) in the z=0 plane as a function of time and radius (and vice versa). The abscissa shows the fraction of the hexa-ammoniate present in the bed*

REFERENCES

[1]   Bach, P.W., J.A. Carp: *Private communication*. 2000.

[2]   Lang, R. et al: *Proceedings ISHPC München*. 1999, p 611.

[3]   Restuccia, G. et al: *Proceedings ISHPC München*. 1999, p 219.

[4]   Goetz, V., B. Spinner: *Proceedings ISHPC München*. 1999, p 591.

[5]   Critoph, R.E. R. Thorpe: *Proceedings ISHPC München*. 1999, p 555.