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# THE SOLID-WATER BOND STRENGTH IN SEWAGE SLUDGE

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The solid-water bond strength in sewage sludge has been studied with two different techniques: thermal analysis and water vapour sorption isotherms. The bond enthalpy as a function of the sludge cake moisture content provides information on the maximum feasible dry solids content in a filtration process. In this contribution some preliminary results will be presented.

## INTRODUCTION

Disposal of (dewatered) sewage sludge on dumping sites and in agriculture is becoming more restricted to severe legislation. Disposal options that are of interest now are combustion and drying of dewatered sludges. Therefore the basic aim of a dewatering process is to achieve dry solids contents as high as possible. Sludge dewatering is one of the most difficult problems in waste water treatment. In the Netherlands sludge is primarily dewatered by filter presses and belt presses. In these types of dewatering equipment, a filtration and expression phase can be distinguished [1]. To get a better understanding of the sludge dewatering process, research on fundamental aspects of sewage sludge dewatering is carried out. This study is part of the larger Dutch research program entitled "Future Treatment for Municipal Waste Water, RWZI 2000". An important part of the study is the characterization of the sludge solid-water bond strength. Knowledge about the sludge solid-water bond strength as a function of the

moisture content gives the possibility to predict the maximum feasible dry solids content in a certain dewatering process. The sludge solid-water bond strength can be obtained from thermal analysis techniques and from water vapour sorption isotherms.

## THE PRESENCE OF WATER

Figure 1 presents schematically the way that water may be present in sludge and sludge cake. In a suspension or in a filter cake one can distinguish a water phase and a floc phase. The flocs are formed from the basic sludge particles, in many cases with the addition of flocculants. Flocculants are used to promote the aggregation of basic particles and in this way improve the release of water from sludges. Flocculants that are usually applied in waste water treatment plants are (i)  $\text{FeCl}_3$ , in combination with  $\text{Ca}(\text{OH})_2$ , or (ii) high cationogenic polyelectrolytes. The mechanical behaviour of flocs in a dewatering process depends on floc properties and conditions of dewatering as well. Floc properties of a given sludge depend on amount and nature of the flocculants. The flocs con-

sist of a skeleton, in which interstitial liquid is present. The properties of the basic sludge particles vary with place, season and conditions in the waste water treatment plant. Basic particles, like microbial cells, or pieces of wood, etc. contain water inside. Further hydration layers may be present at the particle surfaces.

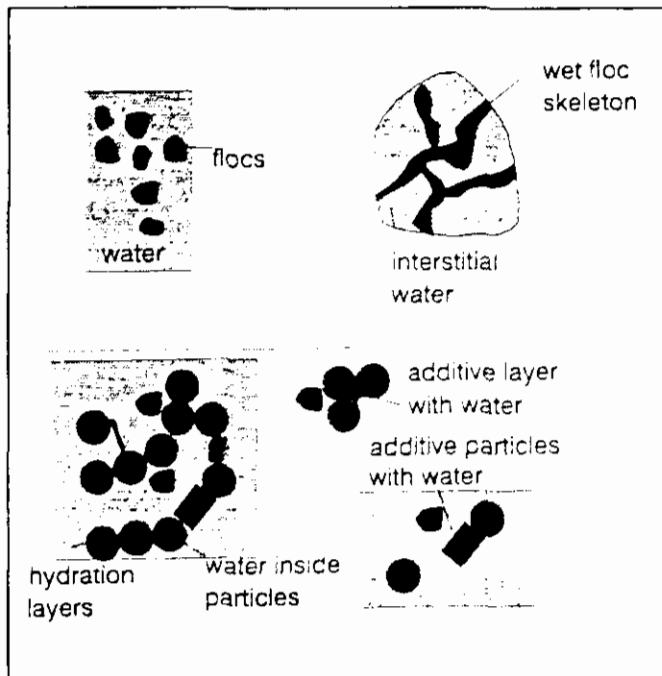


Figure 1. The presence of water in sewage sludge.

THERMAL ANALYSIS: TGA and DTA

With thermogravimetric analysis (TGA) the loss in mass of a sludge cake sample, due to vaporization of water, is measured continuously at a constant temperature. With differential thermal analysis (DTA) the heat flow required for vaporization of water out of the sludge cake sample is measured after calibration [2].

The TGA/DTA equipment gives the possibility to carry out TGA and DTA simultaneously. Knowing the sample moisture content at the beginning of the experiment, moisture content as a function of time can be determined too. The ratio between vaporization rate  $\dot{m}$  (in kg/s), calculated from the TGA-experiments and heat flow to the sample

$q$  (in J/s), obtained from the DTA-experiments, is equal to the heat of vaporization of water  $H_{vap, sample}$  (in J/kg) present in the sample:

$$H_{vap, sample} = \frac{q}{\dot{m}} \quad (1)$$

The heat of vaporization of pure water is a function of temperature according to :

$$H_{vap, water} = H_{vap, water0} - (Cp_w - Cp_{vw}) (T - 273) \quad (2)$$

where:

- $H_{vap, water0}$  = heat of vaporization of water at 273 K [2501 kJ/kg]
- $Cp_w$  = specific heat of water [4.19 kJ/kg·K]
- $Cp_{vw}$  = specific heat of water vapour [1.84 kJ/kg·K]
- $T$  = temperature [K]

The bond enthalpy  $H_b$  (in kJ/kg) is equal to the difference between measured heat of vaporization and heat of vaporization of pure water:

$$H_b = H_{vap, sample} - H_{vap, water} \quad (3)$$

With the TGA/DTA technique the bond enthalpy can be calculated as a function of the sample moisture content.

EXPERIMENTAL

Experiments were carried out with sludge cake samples at constant temperature. Sludge cakes (diameter: 7 cm, thickness: 1 mm) obtained from a filtration cell with a pressure of 3 bar [1]. To improve the dewatering behaviour,  $FeCl_3$  (10 wt% on dry solids basis) in combination with  $Ca(OH)_2$  (20 wt% on dry solids basis) were added to the sludge. In all experiments, secondary sewage sludge, taken from the waste water treatment plant 'De Dommel' in the Netherlands, was used. In figure 2, a result of a TGA/DTA-experiment is given. In this experiment a sludge cake sample, having an initial mass of 32.5 mg and an initial

moisture content of 3.33 kg<sub>water</sub>/kg<sub>dry solids</sub>, was submitted to a constant temperature of 353 K. At the start of the experiment the vaporization rate and heat flow were relatively high. In the first drying stage, rate of vaporization remains constant and free water is transported. In this stage, the heat of vaporization in the sample is equal to the heat of vaporization of pure water. At a sample moisture content of 1.5 kg<sub>water</sub>/kg<sub>dry solids</sub> vaporization rate and heat flow start to decrease and the bond enthalpy differs significantly from zero. It can be calculated that water can not be removed by filtration, when the bond enthalpy is larger than 1 kJ/kg [2]. So, from the graph given in figure 2 the conclusion can be drawn that the maximum feasible dry solids content in a filtration process of this sewage sludge is approximately 40 wt% on dry solids basis.

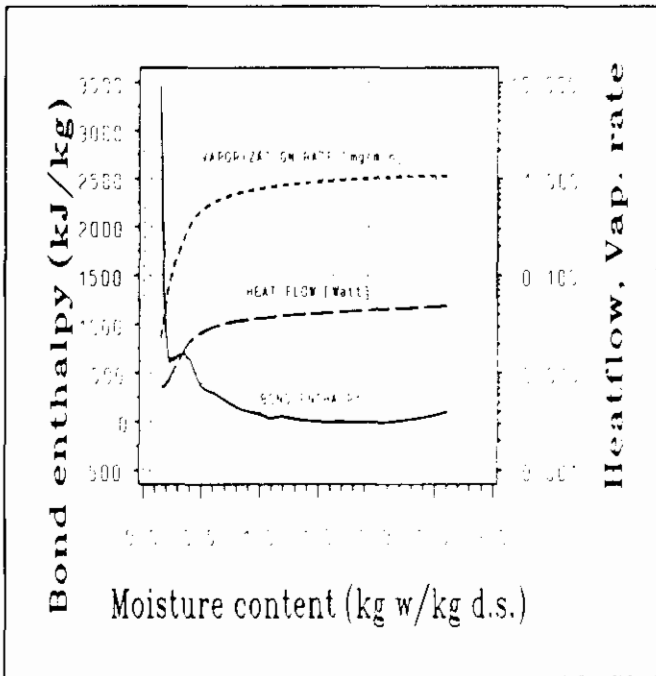


Figure 2. Measured vaporization rate, heat flow and bond enthalpy as a function of the sample moisture content.

WATER VAPOUR SORPTION ISOTHEPMS [3]

Another technique to characterize the sludge-water bond is measuring water vapour

sorption isotherms. A water vapour sorption isotherm of a substance is the constant temperature relation between the amount of water in the substance and its thermodynamic water activity  $a_w$ . Under normal conditions ideal behaviour of the gas phase may be assumed and the  $a_w$  equals the relative humidity of the gas phase. Thus:

$$a_w = \frac{P_v}{P_{w0}} \quad (4)$$

With:

- $p_w$  = water vapour pressure [Pa].
- $p_{w0}$  = saturated water vapour pressure at standard temperature and pressure [Pa].

In case of bond water  $a_w$  will become significantly smaller than 1.  $a_w$  for a certain system is a function of temperature and moisture content ( $0 \leq a_w \leq 1$ ).

In literature about 80 equations to describe sorption isotherms are known [4,5] because the interactions between water (sorbate) and dry substance (sorbent) are very complex. A relative simple sorption model with three parameters is the G.A.B.-model (Guggenheim [6] (1966), Anderson [7] (1946) and de Boer [8] (1953)):

$$\frac{X_v}{X_{w1}} = \frac{C_g k a_w}{(1 - k a_w) (1 - k a_w + C_g k a_w)} \quad (5)$$

with:

- $X_w$  = mass fraction of water on dry solids basis [kg<sub>water</sub>/kg<sub>dry solids</sub>].
- $X_{w1}$  = the amount of sorbate adsorbed when all sites contain one molecule, also named completed monolayer [kg<sub>water</sub>/kg<sub>dry solids</sub>].
- $C_g$  = the Guggenheim constant which depends on the nature of the interaction between sorbate and sorbent and the temperature.
- $k$  = factor which corrects the differences between the properties of water molecules in the multilayer and the properties of pure water.

In this study the G.A.B.-equation will only be used for data reduction and won't be used for physical interpretation.

From water vapour sorption isotherms, measured at different temperatures, the differential enthalpy of wetting can be calculated by application of the Clausius-Clapeyron equation:

$$\left( \frac{\partial \ln a_w}{\partial \left( \frac{1}{T} \right)} \right)_{X_w} = \frac{H_w}{R} \quad (6)$$

where:

- $H_w$  = differential enthalpy of wetting [kJ/kmol]
- $R$  = gas constant [8.31 kJ/kmol·K]
- $T$  = temperature [K]
- $a_w$  = water activity [-]
- $X_w$  = moisture content [kg<sub>water</sub>/kg<sub>dry solids</sub>]

At a given moisture content  $X_w$  the differential enthalpy of wetting can be found by plotting  $\ln(a_w)$  against  $1/T$ . The slope of the straight line is equal to  $H_w/R$ .

#### EXPERIMENTAL [9]

Water vapour resorption isotherms of sludge cake samples were determined with the conventional technique of vacuum exsiccators with saturated aqueous salt solutions to control the water activity. The data for the water activity of these solutions were taken from the tables of Greenspan[10] (1977). For keeping a constant temperature during equilibration the exsiccators were positioned in a thermostated water bath ( $\pm 0.1$  K). Equilibrium was assumed if two subsequent weighings gave the same results.

To obtain sewage sludge cake samples, the same procedure was used as described before. From the obtained sludge cake

twelve samples (mass is about 35 mg) with a diameter of 5 mm and a thickness of 1 mm were taken. The samples were dried in an oven at 383 K during 24 hours.

The twelve dry sludge cake samples were placed in twelve different exsiccators, each with their own water activity. At reaching equilibrium conditions within 24 hours, the moisture content of the samples was determined and the resorption isotherm was constructed. For three temperatures (303, 323 and 343 K) water vapour resorption isotherms were measured.

The G.A.B.-equation is fitted to the measured resorption data using the sum of least-squares method for minimizing the absolute differences between measured and calculated moisture contents  $X_w$ . This was efficiently done by using the Statistical Analysis System package (SAS).

#### RESULTS

Figure 3 shows the experimental data and the fitted G.A.B.-equation for three temperature levels.

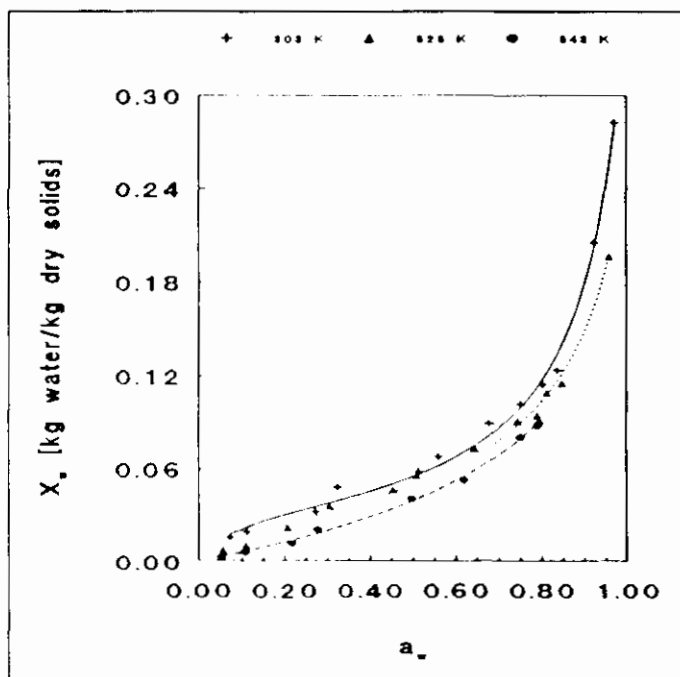


Figure 3. Fitting of the data points with the G.A.B.-equation for the water vapour resorption experiments.

For the whole  $a_w$ -range the G.A.B.-equation

describes the data points very well. In figure 4 the differential enthalpy of wetting  $H_w$  (in kJ/kg<sub>water</sub>) is plotted against the moisture content  $X_w$  (in kg<sub>water</sub>/kg<sub>dry solids</sub>). With these data it was possible to calculate the energy to remove water per kilogram dry solids. The energy needed to reduce the moisture content of a sludge cake from 0.12 kg<sub>water</sub>/kg<sub>dry solids</sub> to 0.01 kg<sub>water</sub>/kg<sub>dry solids</sub> is equal to 320 kJ/kg<sub>dry solids</sub>.

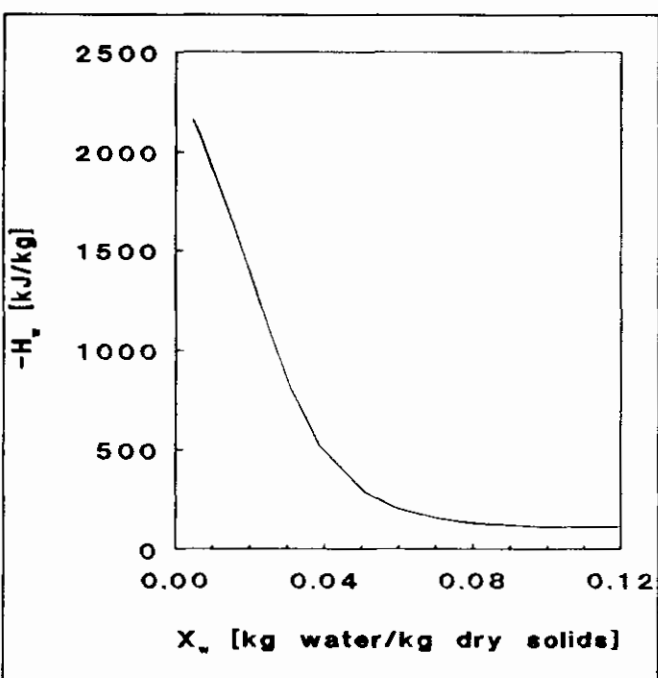


Figure 4. The differential enthalpy of wetting ( $H_w$ )

#### CONCLUSIONS

The TGA/DTA and water vapour sorption isotherms techniques are promising methods for characterization of the solid-water bond strength in sewage sludges. 'Bond water', which is defined as water having a bond enthalpy  $H_b$  larger than 1 kJ/kg [2], cannot be separated in a mechanical dewatering process. It appears from the TGA/DTA result that the amount of 'bond water', present in a sludge cake is equal to 60 wt% on water base. In this preliminary result it is not possible to compare the TGA/DTA and water vapour sorption isotherms results. This is due to the different pre-treatment procedures. The water vapour

sorption isotherm technique will be improved by measuring water vapour desorption isotherms of sewage sludge instead of resorption isotherms.

The water vapour sorption isotherms can be described very well with the G.A.B.-equation.

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#### NOTATION

$a_w$	=	water activity	[-]
$C_g$	=	Guggenheim parameter	[-]
$C_{pw}$	=	specific heat of water	[J/kg·K]
$C_{pww}$	=	specific heat of water vapour	[J/kg·K]
$H_b$	=	bond enthalpy	[kJ/kg]
$H_{vap,sample}$	=	heat of vaporization of water present in sample	[kJ/kg]
$H_{vap,water}$	=	heat of vaporization of water	[kJ/kg]
$H_w$	=	differential enthalpy of wetting	[kJ/kmol]
$k$	=	correction factor	[-]
$\dot{m}$	=	vaporization rate	[kg/s]
$p_w$	=	vapour pressure	[Pa]
$p_{w,s}$	=	saturated vapour pressure	[Pa]
$q$	=	heat transfer rate or heatflow	[J/s]
$R$	=	gas constant	[J/mol·K]
$T$	=	temperature	[K]
$X_w$	=	moisture content	[kg <sub>water</sub> /kg <sub>dry solids</sub> ]
$X_{w1}$	=	monolayer value	[kg <sub>water</sub> /kg <sub>dry solids</sub> ]

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