

# Treatment of Waste Material: Flue Gas Cleaning

## Operational experience with evaporation of washing water from flue gas cleaning in the thermal treatment of industrial waste in the RZR Herten

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The priorities in the waste handling programme of the German Federal Government – prevention, utilisation, disposal – have led to integrated economic management concepts for waste materials. An important aspect of these concepts is the utilisation of residues from thermal and physical-chemical treatment of waste. Evaporation of washing water from flue gas cleaning systems in thermal treatment plants has been carried out for about 10 years.

### 1. Classification of washing water from flue gas cleaning systems

Numerous proven methods are now known for flue gas cleaning [1]. The methods are often classified as dry, quasi-dry and wet absorption [2], the latter now constituting the standard. Wet cleaning of flue gases produces waste water containing chlorides, sulphates, fluorides or the corresponding free acids, always accompanied by heavy metals in various concentrations and ratios.

Table 1 gives an overview of the characteristic main substances present [3]. Methods have been developed for recovering hydrochloric acid from flue gases rich in HCl. The main substances present are derived from the various components of the fuels and the neutralising agent for regenerating the washing solutions. Customary neutralising agents are calcium oxide, calcium hydroxide and chalk, in some instances sodium hydroxide solution, too. Depending on the particular washing method and technology employed, the total concentration of dissolved substances lies in the range from 5% to 20% by weight.

The tolerated concentration is determined among other factors by the required absorption efficiency which falls with increasing loading of the washing solutions. In order not to exceed the maximum allowed concentration in the washing water, effluent streams must be taken from all wet flue gas washing processes and treated as waste water. The classical treatment method is chemical and physical processing of the waste water with the main purpose of removing heavy metals by neutralisation and precipitation [4, 5] before discharging the water. The disadvantage of this classical method is that the neutral salts remain in the treated waste water and, depending on the particular site, contribute to salination of local surface water. To avoid this problem shift from gas discharge to waste water discharge, further waste water treatment methods have been introduced for separating the neutral salts, too [3, 6]. These methods are based on crystallisation by evaporation.

### Concepts for washing water evaporation plants

With regard to the basic principle of utilisation envisaged

by the economic concept of the waste disposal programme, the waste water components (cf. Table 1) should be isolated in a form permitting their re-use as production materials. This cannot be achieved for all substances present. For example, the heavy metal burden can only be separated as unusable mixed hydroxide and sulphide sludges which have to be dumped, after appropriate treatment by neutralisation and dehydration. Implemented evaporation concepts are based on the recovery of calcium chloride as its dihydrate or the recovery of sodium chloride,

depending on the particular neutralising agent used for flue gas cleaning [3, 6].

### Flue gas washing with calcium hydroxide:

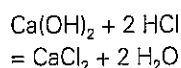
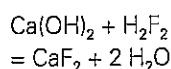
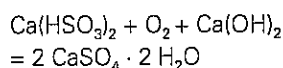
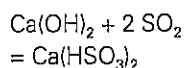
When flue gas washing water is neutralised with calcium hydroxide a suspension is obtained whose main components are the undissolved solids calcium sulphate and calcium fluoride, and readily soluble calcium chloride. After separating the components insoluble in water by filtration and then precipitating and filtering off the heavy metals, a calcium chloride solution saturated

**Table 1:** Composition of various waste solutions from flue gas cleaning plants (main components)

Substance	1	2	3	4	5	6
NaCl	○	○○	○○	○	○	○○
MgCl <sub>2</sub>				○	○○	
CaCl <sub>2</sub>	○○		○○	○○	○○	○
Na <sub>2</sub> SO <sub>4</sub>		○○				

- 1 MVA with calcium oxide wash
- 2 MVA with sodium hydroxide solution wash
- 3 MVA with NaOH wash and Ca(OH)<sub>2</sub> neutralisation
- 4 KW with calcium oxide wash (hard coal)
- 5 KW with calcium wash (soft coal)
- 6 KW with calcium oxide wash and Na<sub>2</sub>SO<sub>4</sub> treatment

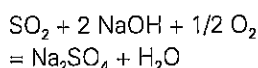
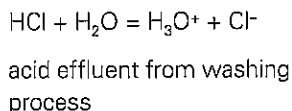
with calcium sulphate remains:



In flue gas cleaning plants after thermal treatment of waste material in which the HCl component in the flue gas exceeds all other components, these solutions contain only small concentrations of other substances such as magnesium chloride and sodium chloride. Here it is expedient to isolate the calcium chloride as technical dihydrate by total evaporation, i.e. by vacuum evaporation crystallisation. This is the procedure in the RZR Herten [7].

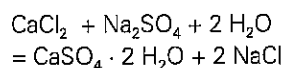
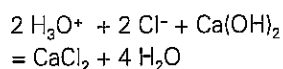
#### Flue gas washing with sodium hydroxide solution and acid prewash:

Washing with sodium hydroxide solution is adopted chiefly for flue gas cleaning in thermal treatment plants for waste materials. The operating costs are higher, but the advantage is that there is no incrustation on the washers. To save sodium hydroxide solution in such flue gas cleaning systems, mainly hydrogen chloride is absorbed and only partially neutralised in a first stage. The remaining pollutant gas components such as sulphur dioxide and hydrogen fluoride are then neutralised with sodium hydroxide solution in a second stage. An HCl acid effluent and a neutral effluent containing chiefly sodium sulphate are produced by washing systems operated in this manner:



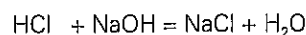
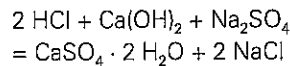
neutral effluent from washing process

Two different possibilities exist for recovering the neutral salts from these effluents. The acid effluent can be neutralised with milk of lime and then combined with the neutral effluent. The sulphate component can then be removed by precipitation of calcium sulphate outside the washer, and after filtration the remaining solution is saturated with calcium sulphate and contains the neutral salts calcium chloride and sodium chloride:



Both neutral salts can be recovered separately from this solution by evaporation crystallisation. It follows from the solubility properties of the system  $\text{CaCl}_2 - \text{NaCl} - \text{H}_2\text{O}$  and the excess of calcium chloride present, that sodium chloride crystallises first on evaporation whereas the calcium chloride remains highly concentrated in the mother liquor. This procedure is implemented in the evaporation plant of the MVA Stapelfeld [8].

By controlled addition of milk of lime to the acid effluent of the washing process it is furthermore possible to limit the amount of calcium chloride formed to the amount required to convert the sodium sulphate produced in the neutral washing effluent to calcium sulphate. The residual hydrochloric acid is neutralised with sodium hydroxide solution. In thermal treatment plants there is always a stoichiometric excess of HCl over  $\text{SO}_2$  in the flue gases (see above).



This operating method produces a solution saturated with calcium sulphate from which exclusively sodium chloride can be isolated by evaporation crystallisation after precipitating the heavy metals. The much finer coprecipitate of calcium sulphate is separated hydromechanically and returned to the calcium sulphate precipitation. Apart from avoiding incrustation of the washers, this procedure has the advantage that sodium chloride can be recovered without also producing other highly soluble salts. Furthermore, this exclusive recovery of sodium chloride is achieved without producing additional neutral salts increasing the unusable salt burden as would result by external addition of precipitating agents (here calcium chloride). This is important with regard to preventing unusable waste material. The extreme demands on purity imposed by the potential customers – e.g. for sodium chloride electrolysis [10] – can be fulfilled only with great effort [11].

## 2. Problem solution in the RZR Herten

The first systems for evaporating washing water from flue gas cleaning facilities were introduced at the beginning of the 1980s in plants for thermal treatment of waste materials. One of these systems is the evaporation plant of the industrial waste combustion unit I in the RZR Herten whose task is to treat the waste water from flue gas washing, neutralised with calcium hydroxide, and various streams of process waste water in such a way that there is no discharged waste water (Fig. 1). At that time the large-scale technical crystallisation of calcium chloride dihydrate was introduced for the first time. Conventional processes for obtain-

ing calcium chloride existed at that time only in the field of soda production based on the principle of multi-stage countercurrent evaporation and production of fused calcium chloride dihydrate at temperatures around 170°C. The melt obtained in this procedure is further processed to solid material by prills or on cooling rollers.

This kind of process management requires high-pressure steam heating and very high quality metallic materials to withstand the corrosive effect of highly concentrated calcium chloride solution at elevated temperatures. For evaporating washing water which is not as well-defined as the solutions from the soda process, the new approach via evaporation crystallisation was introduced primarily to combat the material corrosion risk by permitting recovery of calcium chloride dihydrate at considerably lower temperatures. This procedure does not differ from the conventional ones with which many other products, for example sodium chloride, are obtained by evaporation crystallisation. The state of technology for producing these products was transferred to the first plant for obtaining crystallised calcium chloride dihydrate.

### 2.1. Basic concept for evaporation crystallisation

Examples of the state of technology at that time were plant concepts for large-scale production of sodium chloride from so-called concentrated sea water as implemented in the 1960s and 1970s in several instances on the Persian Gulf (Fig. 2) [12, 13]. The drinking water situation there required industrial production of drinking water on a large scale via multi-stage decompression evaporators in which sea water was evaporated nearly to the point of calcium sulphate saturation and the condensation used as drink-

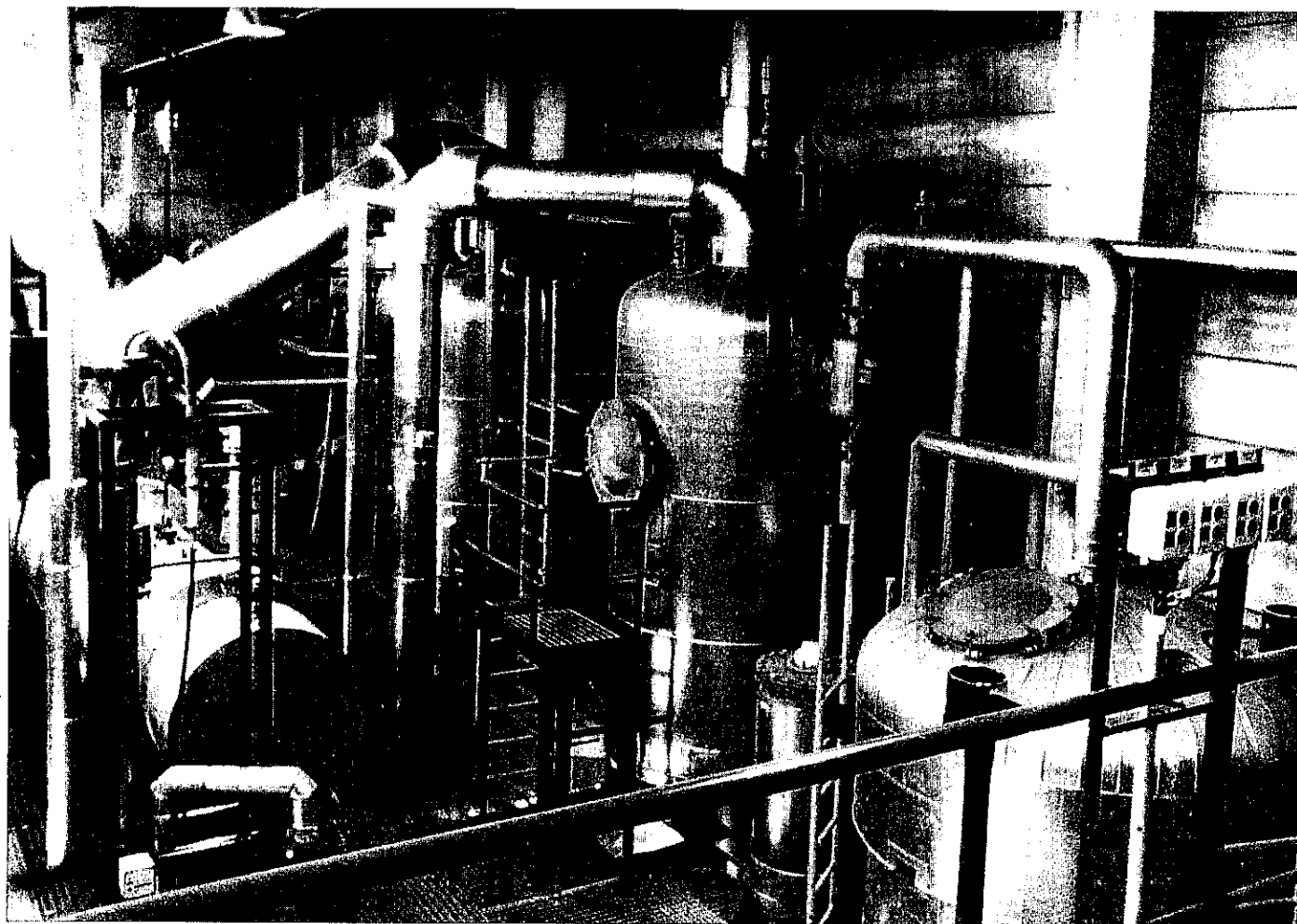


Fig. 1: RZR Herten – Water house

ing water. Most of the brine concentrated to about 6% by weight was returned to the sea, but sodium chloride was obtained from a portion by evaporation crystallisation.

This task, which was solved by multi-stage evaporation plants (Fig. 3) firstly required controlled non-encrusting crystallisation of calcium sulphate because the concentrated sea water was nearly saturated therewith. The solubility of calcium sulphate falls with increasing temperature, so the heating elements are particularly endangered by incrustation. A special seeding technique was developed for these plants to solve the problem by ensuring that the conditions for incrustation cannot arise. This is achieved by retaining the entire precipitated solid calcium sulphate in the particular evaporator stage

and ensuring that the resulting supersaturation can be dissipated very quickly on the suspended crystal mass. This prevents incrustation-producing supersaturation. In the plant shown in Fig. 3 the concentrated sea water is fed into the third stage of the evaporator system in which precipitation does not yet take place. The solution is further concentrated there and then passed to the hot first stage in which crystallisation of calcium sulphate takes place as described above. A multi-cyclone follows after this first stage to separate the produced solid calcium sulphate from the suspension and returns it to this stage. The clear solution is sent to the middle stage in which sodium chloride crystallises. The salt is firstly washed in the following separating station by countercurrent operation,

isolated in a centrifuge and then passed on for electrolysis. The quality of the salt produced in this manner is shown in Table 2.

Three plants with evaporation capacities up to 150 t/h were installed according to this concept. The non-stop running times of these plants are 6 months and not restricted by incrustation. Calcium sulphate incrustation is avoided completely. Sodium chloride incrustation in the second stage is avoided by prophylactic rinsing implemented by adding water for short-term undersaturation at predefined time intervals during running operation.

**Table 2:** Sodium chloride obtained by evaporating concentrated sea water (Persian Gulf)

Grain Size Analysis (RRSB)

$d' = 0.5 \text{ mm}$   
 $n = 3.5$

Chemical Composition: (on TS)

NaCl	99.85	mass %
CaSO <sub>4</sub>	0.07	mass %
MgCl <sub>2</sub>	0.05	mass %
MgSO <sub>4</sub>	0.02	mass %
Moisture	< 0.10	mass %

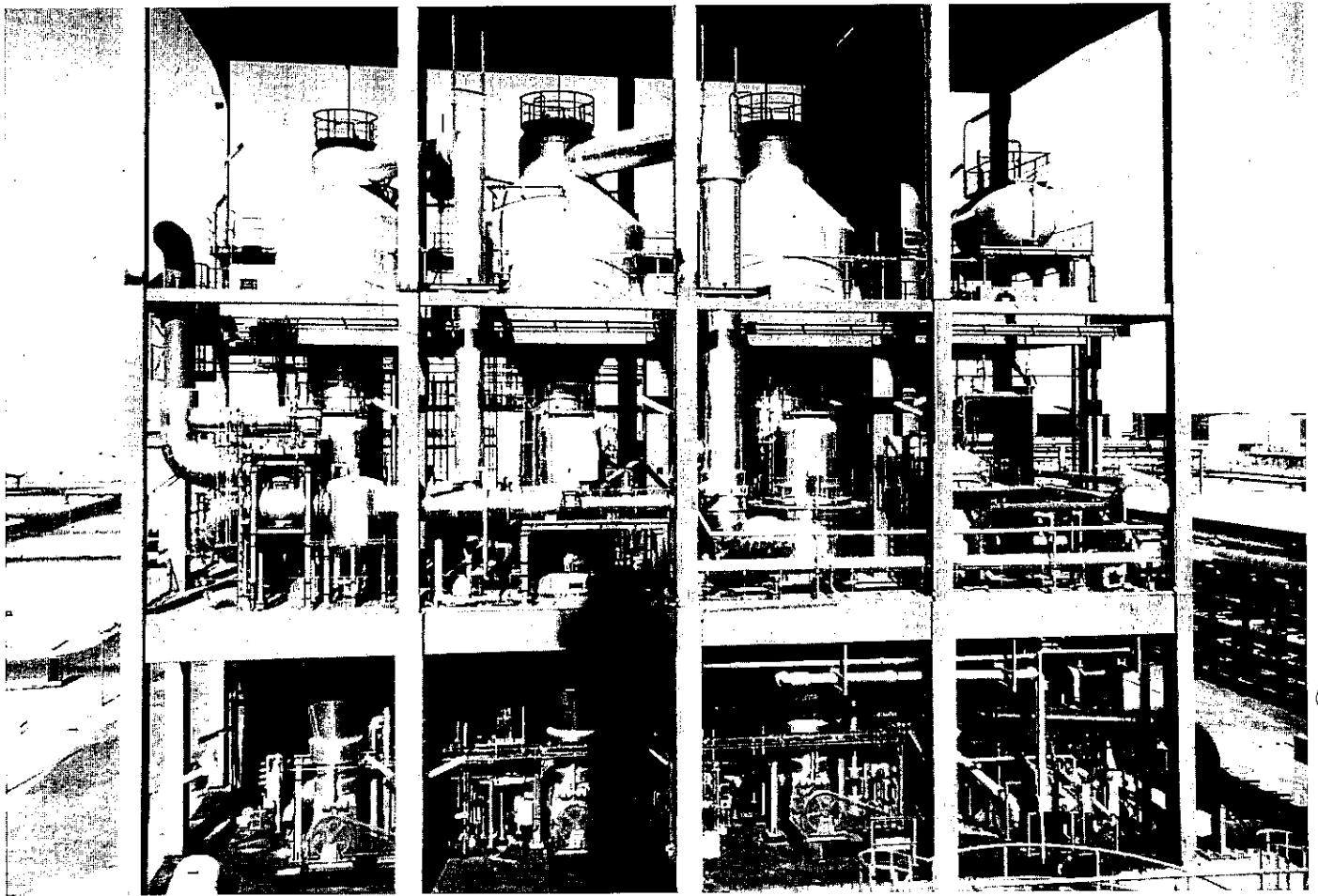


Fig. 2: Electrolysis salt production in Abu Dhabi, U.A.E.

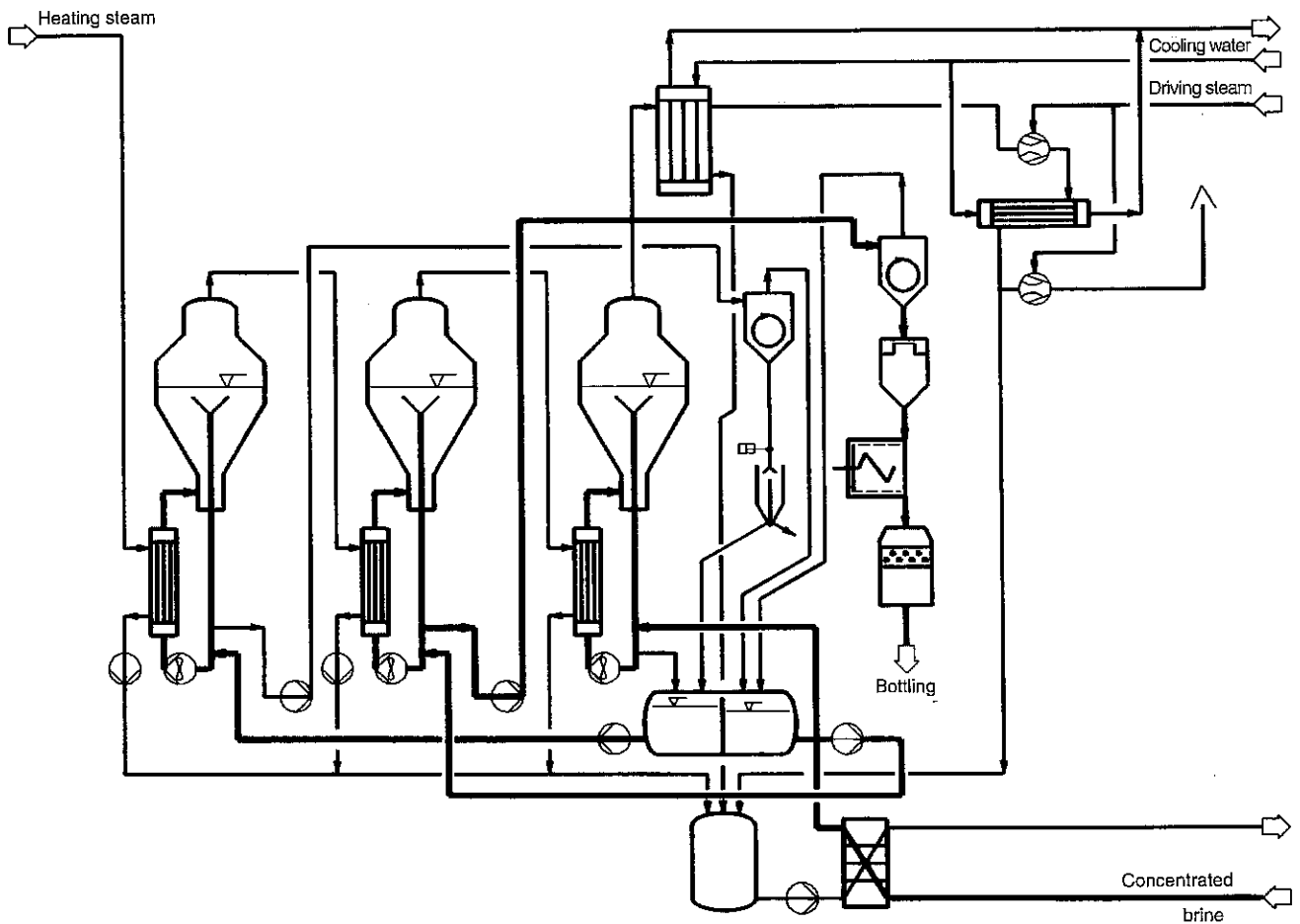


Fig. 3: Schematic diagram of the electrolysis salt production plant in Abu Dhabi, U.A.E.

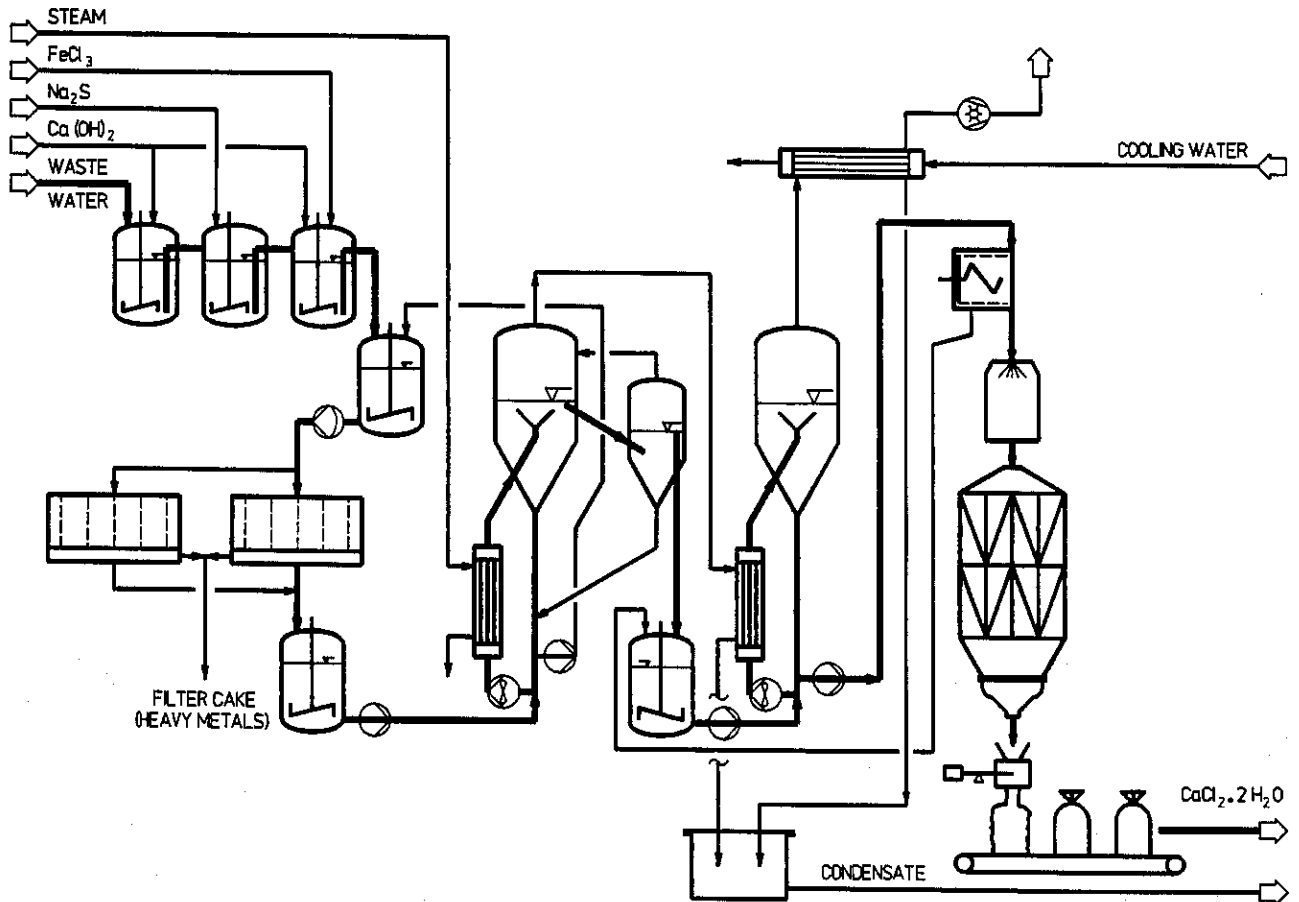


Fig. 4: Schematic diagram of the evaporation plant Herten I

## 2.2. Installed plants

Evaporation of waste water from flue gas washing requires a comparable technology in all aspects. The waste water is concentrated similarly to the concentration of sea water mentioned above, and calcium sulphate appears as the first solid substance during evaporation. However, there are some important differences:

- Waste water from flue gas washing in plants for thermal treatment of waste materials are loaded with impurities such as heavy metals, higher halides, sulphur-nitrogen compounds and sulphur compounds in various oxidation states.

- Since this waste water must be evaporated to dryness, crystallisation can be utilised only for solidification but not for purification unless an effluent solution is tolerated which must be subjected to an additional evaporation process to give unusable residual sub-

stances which must be dumped.

Two evaporation plants were installed in the last decade for waste water from flue gas washing and other process waste water from the industrial waste material lines of the RZR Herten. Both plants are designed for operation without discharged waste water and for recovering industrially usable hydrated calcium chloride. In order to fulfil the quality requirements for this product, the water must be pretreated to remove heavy metals before evaporation. The resulting plant concept is shown in Fig. 4 and corresponds to the first evaporation plant implemented in 1981 in the RZR.

In a continuously operated three-stage agitated boiler cascade the heavy metals are firstly removed from the solution fed in. For this purpose the pH value of the waste

water is shifted to the alkaline range in the first stage of the cascade by adding milk of lime. Flue gas calcium sulphate is added at the same time to bring the waste water, which is still supersaturated with calcium sulphate, to saturation in order to avoid calcium sulphate incrustation during subsequent filtration of the heavy metals precipitate. The heavy metals are precipitated in the second stage of the cascade by adding sodium sulphide solution. In the final stage, the excess precipitating agent is bound by adding ferric chloride which also acts as a coagulating agent. The suspension formed is separated in two alternately operating chamber filter presses. The filter cake is dumped whereas the purified solution runs into a storage tank which continuously feeds the evaporating plant.

The evaporating plant is a two-stage cocurrent vacuum evap-

oration system with forced recirculation crystallisers whose first stage is operated with low-pressure steam heating. Pipe bunch heat exchangers as customary for industrial crystallisation processes are used as heating elements. The vapours from the first stage are used to heat the second stage, whose vapours in turn are condensed indirectly in a cooling system circuit. The non-condensable gases are withdrawn via a vacuum pumping station. The vapour condensation from stage 2 and the final condenser are re-used in the flue gas washing process.

The heavy metal-free solution saturated with calcium sulphate is firstly concentrated in the first evaporating stage. This produces solid calcium sulphate so that adequate crystal suspension density must be ensured here as already in the neutralisation process in order to avoid

incrustation of the heat exchanger. In this plant, a static thickener is provided to retain the solid calcium sulphate, removing the crystalline fraction from the pre-concentrated solution before it runs over into the receiver for the second evaporation stage. The crystalline fraction is returned to the first stage. In the second evaporation stage the solubility limit of calcium chloride is exceeded by further evaporation so that calcium chloride dihydrate crystallises out. This is a normal mass crystallisation process, but some special features exist on account of extreme properties of calcium chloride such as the large elevation of the boiling point, high solubility, rather strong corrosive action and – of special significance for the subsequent drying treatment – strong hygroscopic behaviour. The large boiling point elevation restricts the number of evaporation stages, which is the reason why the system has only two stages. The hygroscopic behaviour makes it necessary to condition the dryer intake air to avoid moistening instead of drying the product. The final product is filled into 25 kg bags.

### 3. Operating experience

The first of the two evaporation plants in the RZR Herten was commissioned in 1981 so that 10 years of operating experience has been gathered in the meantime. This experience has already been used for making many detailed improvements when the RZR Herten was extended with a second industrial waste combustion line in 1989.

#### 3.1. Product quality and marketing

In contrast to conventional market expectations of potential customers, the product appears in crystalline form and not as flakes. The physical consistency of mass crystallisates is generally character-

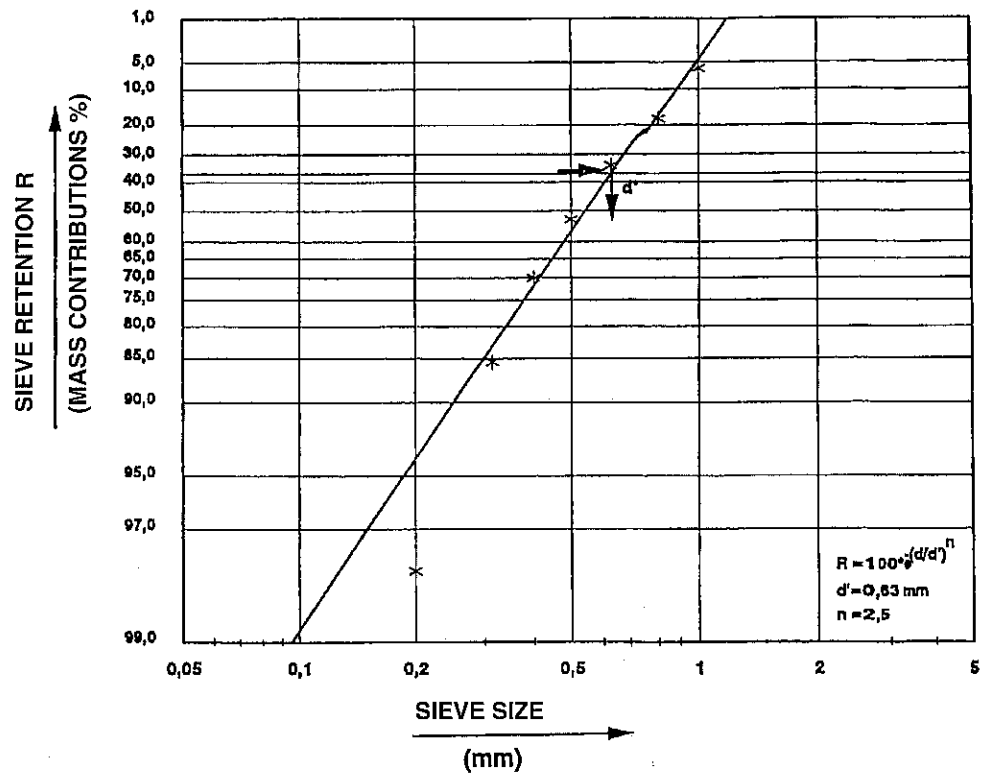


Fig. 5: Grain size distribution in the calcium chloride hydrate

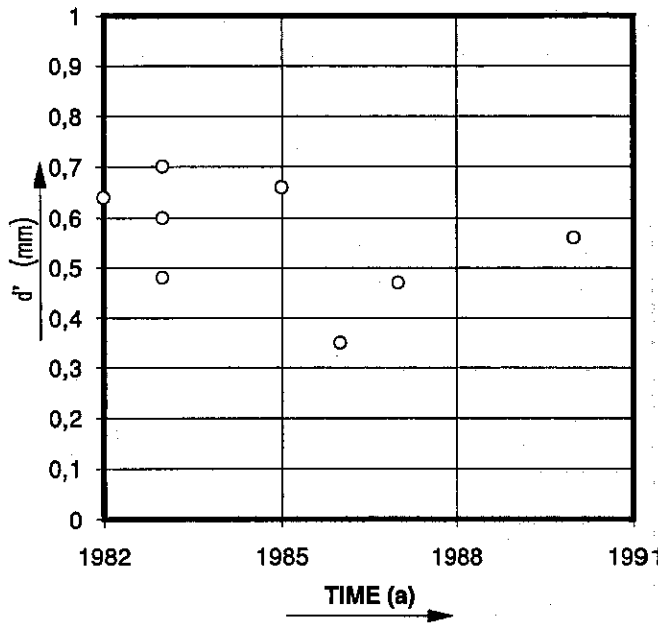


Fig. 6: Grain size distribution from 1982 to 1991

ised by the grain size distribution. Fig. 5 shows a typical distribution of the resulting product according to Rosin-Rammler-Sperling-Bennett (RRSB distribution). The average grain size of  $d' = 0.63$  mm and the uniformity  $n = 2.5$  of the distribution are comparable with corresponding values

for crystallised sodium chloride. The sifting behaviour of the product is excellent provided that it is handled properly in relation to its strongly hygroscopic nature. The operating mode of the industrial waste combustion process evidently has an effect on the grain size distribution of the

product, as evident from an overview of the various measurement readings over the operating years of the plant (Fig. 6), but this does not impair quality.

Product purity essentially conforms to the accepted standard for technical products. The main impurities are listed in Table 3. In particular, production-specific amounts of higher halides (bromide, iodide) as well as boron and nitrogen compounds make it more difficult to market the produced salt. The concentration of subsidiary salts could be reduced with additional plant complexity and solution effluent from the crystallisation process. Fig. 7 gives an overview of the product sales since 1988, showing that marketing of the salt in the amounts produced so far is basically possible. However, this does not clearly show the predicament of the operator of a waste combustion plant faced with the disposal compulsion for a running plant and the statutory re-utilisation decree on a free market. This

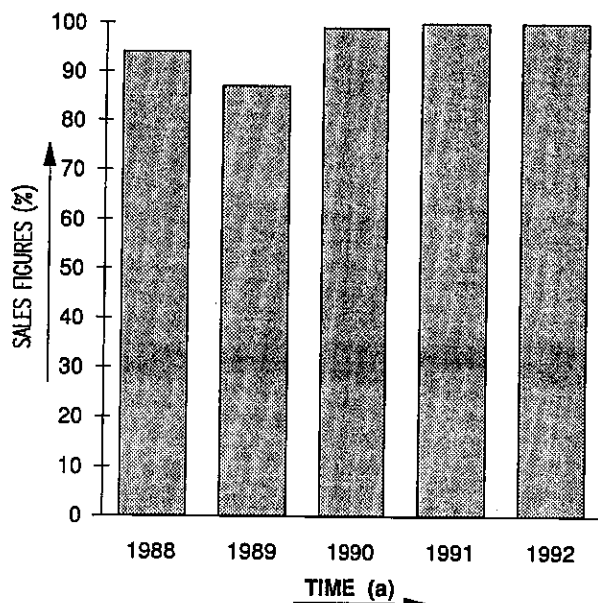


Fig. 7: Sale of the product 1988 to 1992

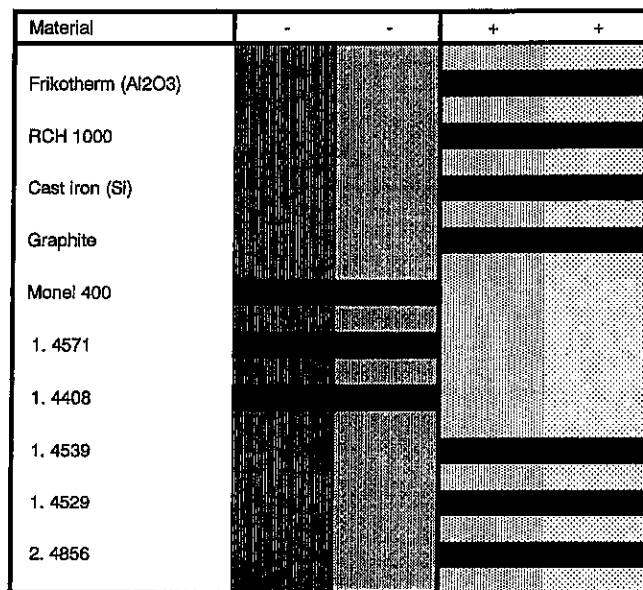


Fig. 8: Experience with materials

**Table 3:** Typical analysis of calcium chloride hydrate

Substance	%
Ca	28.90
Na	2.42
Mg	1.23
Mn	< 0.005
Ba	< 0.001
Fe	< 0.002
Pb	< 0.001
Zn	< 0.001
Cd	< 0.0001
Cu	< 0.001
Ni	< 0.00005
Co	< 0.001
Hg	< 0.00005
As	< 0.0005
NH <sub>4</sub>	< 0.01
Cl	47.30
F	< 0.01
SO <sub>4</sub>	< 0.28
NO <sub>3</sub>	< 0.02

dilemma and the acceptance problems are the chief factors which make it difficult to sell the product under normal market conditions. Attempts to improve the marketability by offering a 30% calcium chloride solution have been abandoned in the meantime.

### 3.2. Experience with materials

Experience with materials was not positive to the same extent at the outset. It was found that the corrosive behaviour of washing water is not comparable to that of constant composition solutions from industrial production processes. The material NiCu30Fe (known as Monel) failed very soon by pitting corrosion when used for the heat exchangers and various other equipment parts, although this material is used successfully in comparable industrial processes. It was not possible to discover the reason for the corrosion unambiguously because, even when using original solutions and comparable mechanical stress conditions, it was not possible to

reproduce the effect under laboratory conditions. On the basis of this experience, graphite heat exchangers have been used successfully since 1987. Highly alloyed stainless steels and alloys based on nickel are only moderately resistant to corrosion and are therefore used only for equipment parts which must be metallic. In contrast, non-metallic materials (Fig. 8) have turned out to be very satisfactory, in particular ceramic linings in the region of salt slurry transportation.

### 3.3. Plant availability

Continuous availability is certainly the most important aspect of a total evaporation system installed at the end of a process designed to run without discharged waste water. Failure of this system for a lengthy period enforces shutdown of the complete plant. Fig. 9 shows the actual availability of the evaporation systems Herten I and II since 1987. Initial process engineering problems, in particular functionally correct dosing of reagents for heavy metal pre-

cipitation and operational disturbance through calcium sulphate incrustation on the filter presses, were solved by minor process modifications. Material problems encountered were remedied by using graphite heat exchangers and pipelines made of material 1.4539, so that the plant concept is now proven.

### 4. Summary

Systems for total evaporation of waste water from flue gas washing in plants for thermal treatment of waste materials have now been in operation for about 10 years. Apart from ensuring operation without discharged waste water, the basic concepts are designed to recover re-usable solid materials in accordance with the Federal Government's economic programme for handling waste material. Known re-usable substances obtained from such evaporation systems are sodium chloride and calcium chloride. Which of these products can actually be obtained also depends on the concept of the flue gas washing process.

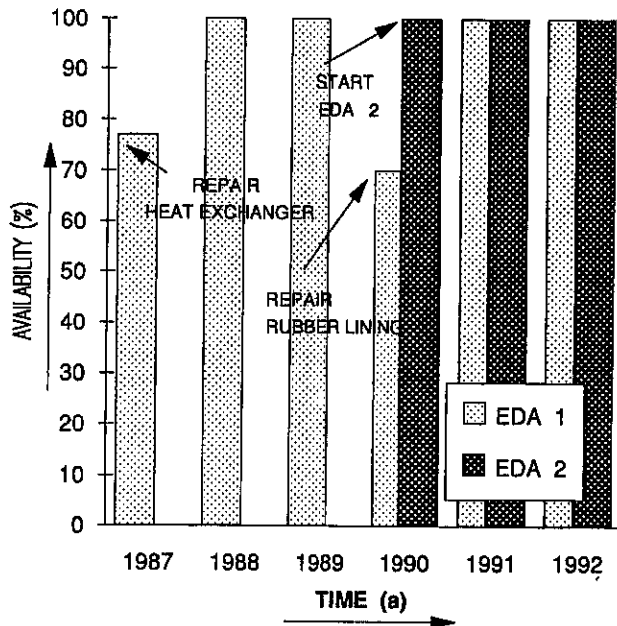


Fig. 9: Availability of the evaporation plants Herten I, II from 1987 to 1992

Two washing water evaporation plants producing calcium chloride are operating in the RZR Herten. The first of these plants was commissioned in 1981 and a second plant followed in 1989 after extending the industrial waste combustion facilities with a second line. The concept of these plants is identical to that of conventional vacuum evaporation crystallisation plants whose state of technology was transferred to the washing water evaporation process. An important aspect for reliable functioning of these plants is the management of calcium sulphate crystallisation without incrus-

tation. Calcium sulphate is the first solid to appear when evaporating waste water saturated therewith. Calcium chloride is isolated from the washing water in technical quality after first removing the heavy metals.

Marketing of this product under acceptable conditions entails several problems. Apart from some process engineering difficulties, chiefly material problems were initially encountered.

The material NiCu30Fe (Monel) failed. Various non-metallic materials are particularly durable. The plant concept is very satisfactory regarding availability.

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