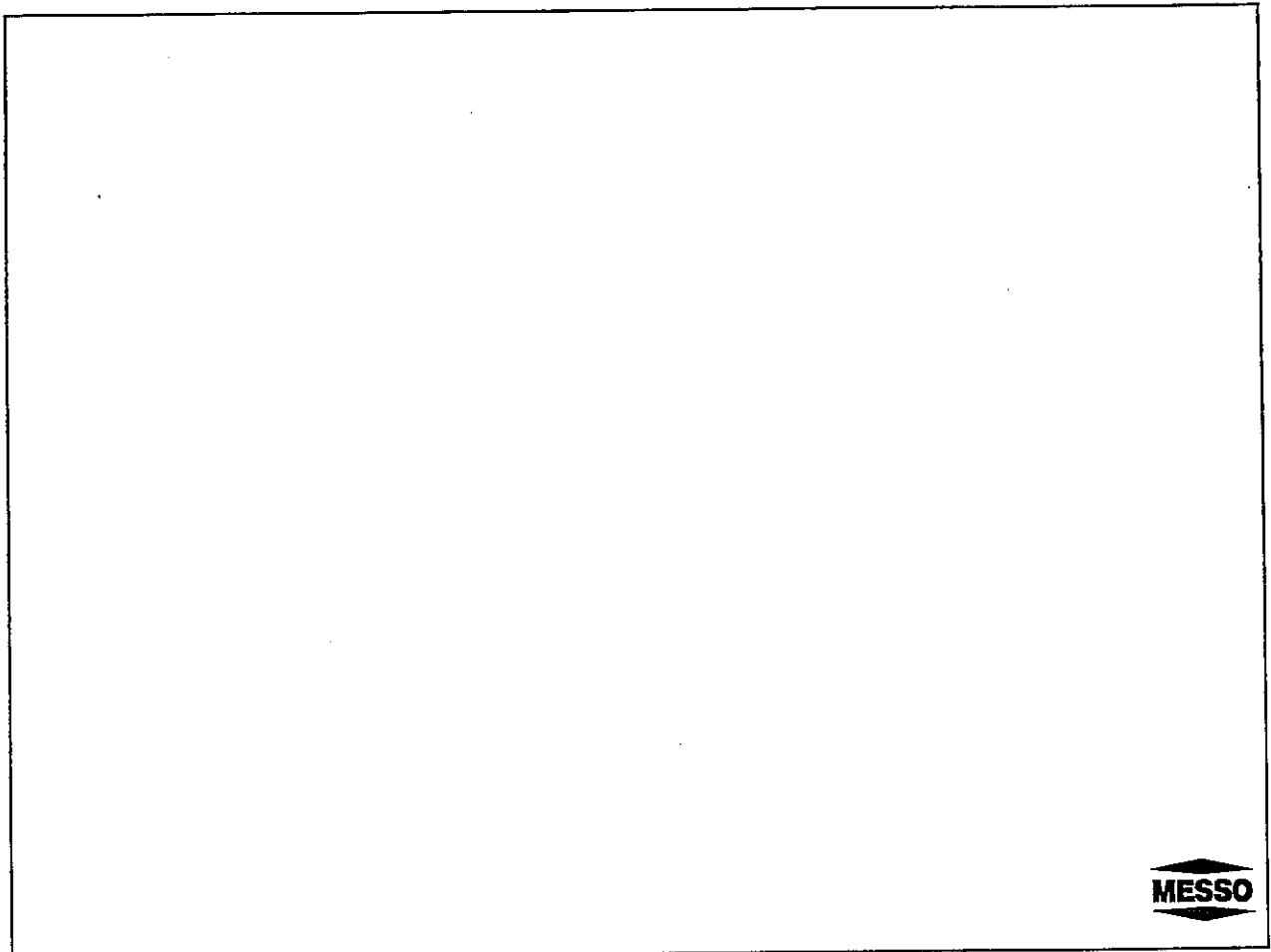


Operational experience gained in the evaporation of scrubber liquors from flue gas purification in the thermal treatment of industrial waste in the RZR Herten centre

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1. The importance of waste water evaporation in the thermal waste treatment

The priorities of the waste management programme of the Federal Government - avoidance, utilization, disposal - have led to the development of integrated waste management schemes which include as an essential element the utilization of the residues resulting from the thermal and chemo-physical treatment of waste. For about 10 years now industry has pursued this object by employing the technology of evaporation of the scrubber liquors from waste gas purification systems forming part of facilities for the thermal treatment of waste.

2. Classification of scrubber liquors from waste gas purification plants

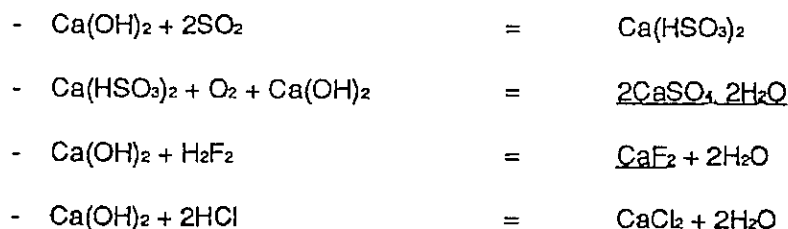
A variety of processes has proved suitable for waste gas purification [1]. In the wet scrubbing of waste gases the produced waste waters contain chlorides, sulphates, fluorides or the corresponding free acids and always also heavy metals. Table 1 shows a compilation of the characteristic main components [2]. The concentration of dissolved substances ranges between 5 and 20 wt.-%. The classical treatment method in these cases is the chemo-physical waste water processing [3, 4]. A drawback of this approach is that the neutral salts remain in the treated waste water. To avoid this mere shift of the problem from the waste gas to the waste water side, more extensive waste water treatment methods have been applied [2, 5]. The process employed in such cases is the evaporative crystallization.

2.1 Designs for scrubber liquor evaporation plants

With a view to the utilization principle, the waste water components should be separated in such a manner that their recycling as a valuable product is possible. This target cannot be reached for all components, however. The heavy metals, for example, can only be separated as hydroxide and sulphide slurries and need to be dumped. Evaporation designs that have already been put into effect are based on the recovery of calcium chloride or sodium chloride [2, 5].

Waste gas scrubbing with lime hydrate:

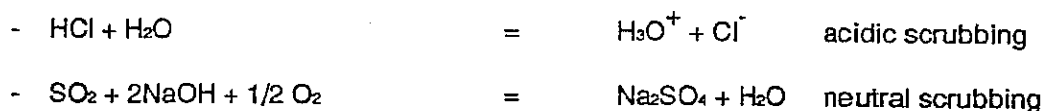
The neutralization of the waste gas scrubber liquor by means of lime produces a suspension which consists of the undissolved precipitate calcium sulphate (gypsum) and calcium fluoride as well as the highly soluble calcium chloride. The substance obtained after filtration and subsequent precipitation and filtration of the heavy metals is a gypsum-saturated calcium chloride solution:



In this case there is the opportunity to separate the calcium chloride by vacuum evaporative crystallization as technical calcium chloride, as this is actually done in the RZR Herten centre [6].

Waste gas scrubbing with soda lye and acidic pre-scrubbing:

Using soda lye for the scrubbing operation is encouraged by the fact that the scrubbers can be operated with hardly any incrustations. The product from such a scrubbing process are a HCl-acidic and a mainly sodium sulphate-rich drain solution:



For these drain solutions there are two possible ways of recovering the neutral salts. By neutralizing the drain solution from acid scrubbing with lime milk and subsequent mixing of the two drain solutions, the sulphate component can be separated by scrubber-external precipitation of gypsum. The solution obtained after filtration is gypsum-saturated and contains the neutral salts calcium chloride and sodium chloride:



This mode of operation is actually applied in the MVA Stapelfeld evaporation plant [7]. As a second method based upon this one, the controlled addition of lime milk to the drain solution of the acidic scrubbing process allows a restriction of the developing portion of calcium chloride to the quantity required to transform the portion of sodium sulphate, which has formed in the neutrally controlled scrubbing process, to gypsum. The remaining hydrochloric acid is neutralized with soda lye:



This mode of operation [8] produces a gypsum-saturated solution, from which - after precipitation of the heavy metals - only sodium chloride can be separated by evaporative crystallization. It is important to stress, moreover, that this exclusive aiming at sodium chloride is possible without an additional formation of neutral salts, i.e. increase of the non-utilizable salt burden, as it would be the case by external addition of precipitating agents (in this case calcium chloride). With a view to the waste avoidance directive this is of significance as up to this day the utilization of the produced sodium chloride is not ensured. The extremely high purity demands of the potential customers [9] are hard to fulfill even with large expenditure [10].

3. Approach in the RZR Herten centre

The first plants for the evaporation of scrubber liquors from waste gas purification plants were erected in works for the thermal treatment of waste in the early Eighties. One of them is the evaporation plant of the industrial waste incineration No. 1 in the RZR Herten centre (Fig. 1). This evaporation plant was at that time the first large-scale facility for the crystallization of calcium chloride dihydrate. The process does in no way differ from the conventional crystallization methods used to recover a lot of other products, e.g. common salt. The state of the art then reached in the recovery of these products was fully integrated in the design of this first plant for the production of crystallized calcium chloride dihydrate.

3.1 Plants so far erected

The evaporation of waste waters from waste gas scrubbing plants, nevertheless, reveals the following important differences:

- The waste waters from waste gas scrubbing facilities in plants for the thermal treatment of waste are burdened with ever changing impurities such as heavy metals, bromine and iodine, sulphur nitrogen compounds and sulphur compounds in various valence states.
- The evaporation of these waste waters must reach the dry state, i.e. the crystallization can be utilized as a consolidation process only and not as a purification process, if a solution discharge is to be avoided, which would have to be subjected to an additional evaporation for dumpable residues.

In the last decade two evaporation plants were erected for the waste waters of the industrial waste lines of the RZR Herten centre. The two plants are designed to ensure the waste water free operation of the incineration plants and to produce a usable technical calcium chloride. The respective plant design is shown in Fig. 2; it corresponds to the first evaporation plant erected in the RZR centre in 1981/1982.

First, a continuously operated agitated-vessel cascade serves to remove the heavy metals from the solution. For this purpose, in the first stage, lime milk is added to take the pH value to the alkaline range. In the second stage of the cascade the addition of sodium sulphide solution leads to the precipitation of the heavy metals, and in the last stage the excess quantity of precipitating agent is bonded by adding iron(III) chloride, which simultaneously serves as a flocculation aid. The produced suspension is separated via chamber filter presses. The filter cake is dumped, while the purified solution is fed to the evaporation plant. The evaporation plant is a two-stage forward-feed vacuum evaporation in forced-circulation crystallizers. The non-condensable gases are withdrawn via a vacuum pump station. The vapour condensate is re-used in the waste gas scrubbing process. In the first evaporation stage a calcium sulphate precipitate is formed so that it is necessary to ensure a sufficient crystal suspension density in order to prevent incrustations of the heat exchanger. A static thickener is employed for this purpose. The crystallized mass is returned to the first stage, the solution flows over to the second stage. In the second evaporation stage, calcium chloride dihydrate is crystallized. Peculiarities may be given by some extreme substance values of the calcium chloride. The high boiling-point elevation restricts the number of evaporation stages, which is reflected by the two-stage feature of the plant. Hygroscopicity makes the conditioning treatment of the dryer intake air compulsory, if a moistening effect instead of the desired drying of the product is to be prevented.

4. Experience gained in their operation

The first of the two evaporation plants in the RZR Herten centre was commissioned in 1981/82 so that meanwhile the experience of 10 years of operation has been collected. This experience was already utilized when the RZR Herten centre expanded by a second industrial waste incineration line in 1989 including a second evaporation line.

4.1 Product quality and marketing

The product is recovered as a crystallized mass. The free-flowing property of the bulk is excellent, as long as a substance-adapted treatment regarding the pronounced hygroscopicity is ensured. Obviously, the operation of the industrial waste incineration has an influence on the particle-size distribution of the product (Fig 3); effects on the operation and the product quality, however, are not perceptible. The product purity generally corresponds to the standard applicable to technical products. The main components are shown in Table 2. Particularly, its content of bromine and iodine as well as boron and nitrogen compounds makes it difficult to market the produced salt. Fig. 4 informs about the product's sales figures since 1988. It shows that the marketing of the salt in the quantities produced so far is generally possible. It does not show, however, the problematic situation of the operator of an incineration plant, who is confronted with a free market when facing the disposal necessity of a running plant on the one hand and the utilization directive of the legislation on the other hand. This dilemma and the acceptance problems render its selling at usual market conditions difficult.

4.2 Experience gained about materials used

It was shown that the scrubber liquors regarding their corrosive behaviour are not comparable with constant-composition solutions from production processes. The material NiCu30Fe failed due to pitting corrosion, although it has been successfully used in comparable processes. Since 1987 the material successfully used for the heat exchangers is graphite. High-alloy stainless steels and nickel-based alloys have proved moderately stable. The best performance has been shown by non-metal materials (see Fig. 5), particularly ceramic pumps for salt slurries.

4.3 Availability of the plants

Fig. 6 shows the availability of the evaporation plants Herten I and II since 1987. Initial process-related problems, especially the function-adapted proportioned feeding of reagents for the heavy metal precipitation as well as functional disturbances by gypsum incrustations on the filter presses, were solved by slight modifications of the process technique. Problems with materials were solved particularly by using graphite heat exchangers and pipes made of material 1.4539, so that meanwhile the plant design can be considered time-tested and reliable.

5. Summary

Evaporation plants for the overall evaporation of waste waters from waste gas scrubbing downstream of plants for the thermal treatment of waste have been in operation now for about 10 years. Apart from ensuring the waste water free operation, the designs aim at the recovery of reusable substances. In the RZR Herten centre, two scrubber-liquor evaporation plants producing calcium chloride are in operation. The first one of these plants was commissioned in 1981, a second one followed in 1989. The design of these plants is identical with conventional plants of vacuum evaporative crystallization. Of utmost importance is the incrustation-free control of the crystallization of calcium sulphate, which is produced as first precipitate in the evaporation of the gypsum-saturated waste waters. The calcium chloride of the scrubber liquors is separated in technical quality after a previous separation of the heavy metals. The marketing of the product at reasonable conditions is problematic. At the beginning there were process-related difficulties and, above all, problems with the materials employed. The material NiCu30Fe failed. Meanwhile, various non-metal materials have proved particularly long-lasting. With regard to the plant's availability the design has been reliably time-tested.

6. Literature

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- (2) Hofmann G., Schmitz R., Wöhik W.: BWK 42 (1990) 3, 116/123
- (3) Gutberlet H.: VGB Kraftwerkstechnik 64 (1984) 1, 41/49

- (4) Schönbacher B., Dieterle E.: VGB Kraftwerkstechnik 64 (1984) 8, 679/688
- (5) Neumann J.C., Hofmann G.: BWK 37 (1985) 9, 352/355
- (6) Bauschlicher H. et al.: DE-PS 36 34 666
- (7) Schmidt R.H.: Phoenix Int. 1(1983) 2, 10/15
- (8) Hofmann G. Schmitz R., Wöhlk W.: DE-PS 39 20 544
- (9) VKE / TAKE (Technical Workpool Electrolysis in the association of the German plastics-producing industry)
- (10) Enders R., Vater C., Jekel M.: Müll und Abfall, Heft 8 (1991)

- Fig. 1** One of them is the older one of the two evaporation plants in the RZR Herten centre; its purpose is to process the waste waters of the lime-controlled waste gas scrubbing in a completely waste water free mode of operation (Fig. 1)
Title: RZR Herten centre - water house
- Fig. 2** The plant design derived from this is shown in Fig. 2 and corresponds to the first evaporation plant commissioned in the RZR centre in 1983.
Title: Flow diagram of the Herten I evaporation plant
- Fig. 3** ... only slight influence on the particle-size distribution of the product, as a compilation of the various measuring values over the years of the plant's operation demonstrates (Fig. 3).
Title: Particle-size distributions from 1983 to 1992
- Fig. 4** Fig. 4 shows the sales figures of the product over the years of operation till today and definitely confirms that the underlying waste water processing design is appropriate.
Title: Sales figures of the product from 1988 to 1992
- Fig. 5** Non-metal materials, on the other hand, proved an outright success (see Fig. 5)
Title: Experience gained with materials
- Fig. 6** Fig. 6 shows the availability of the Herten I and II evaporation plants over the years of operation since 1987.
Title: Availability of the Herten I and II evaporation plants from 1987 to 1992
- Table 1** Table 1 shows a compilation of the characteristic main components [3]
- Table 2** The product purity essentially corresponds to the standard applicable to technical products. The main components are shown in Table 2.
Title: Analysis of calcium chloride hydrate

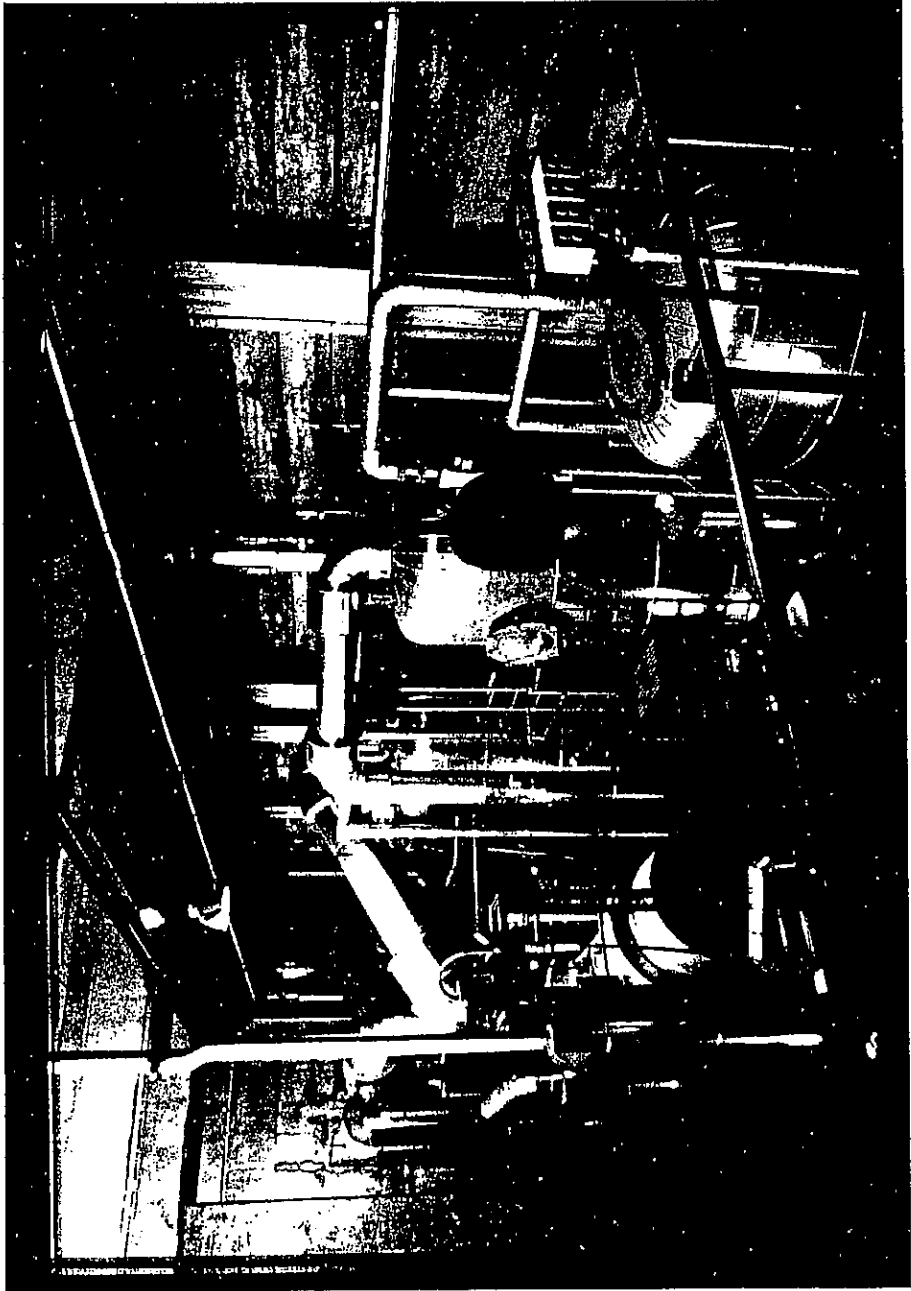
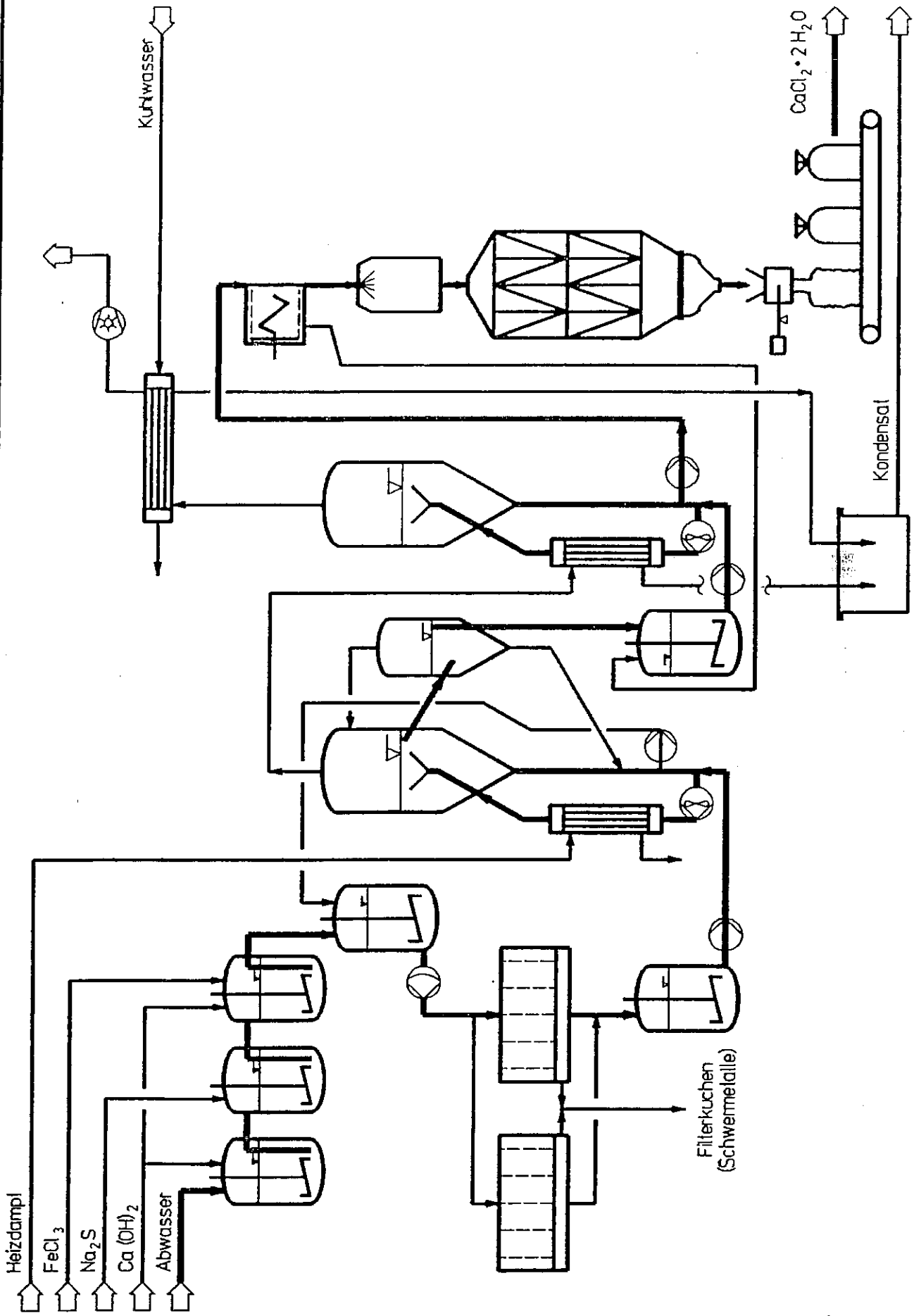


Fig. 1
RZR Herten centre - water house



Schallschema Eindampanlage Herten I

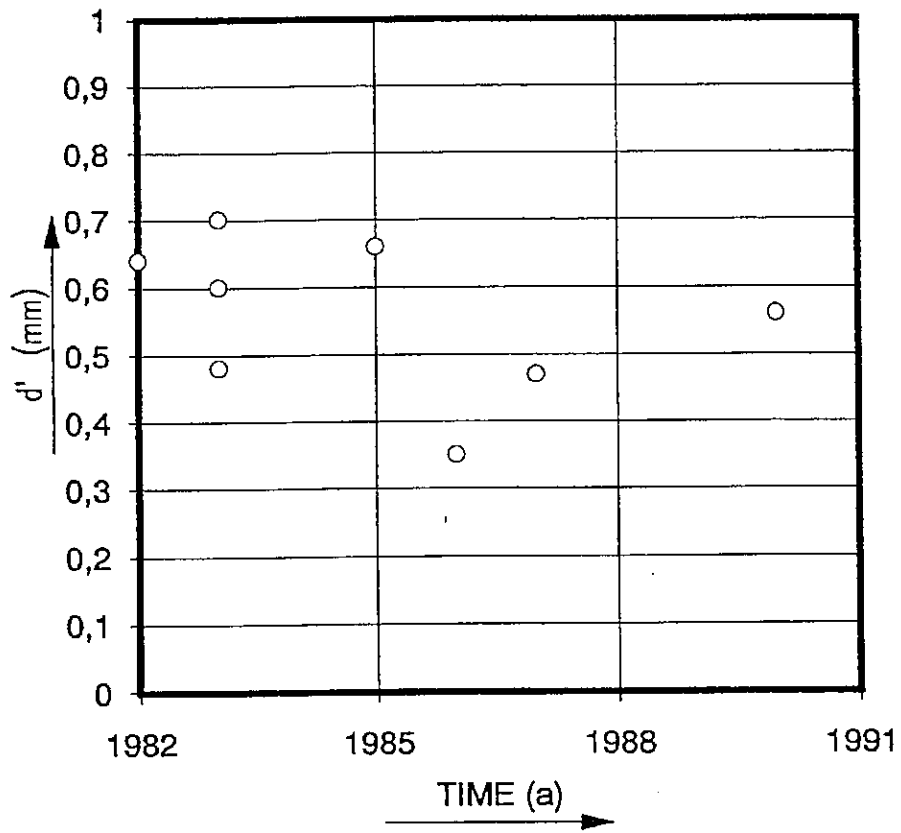


Fig. 3
Particle size distributions 1982 - 1991

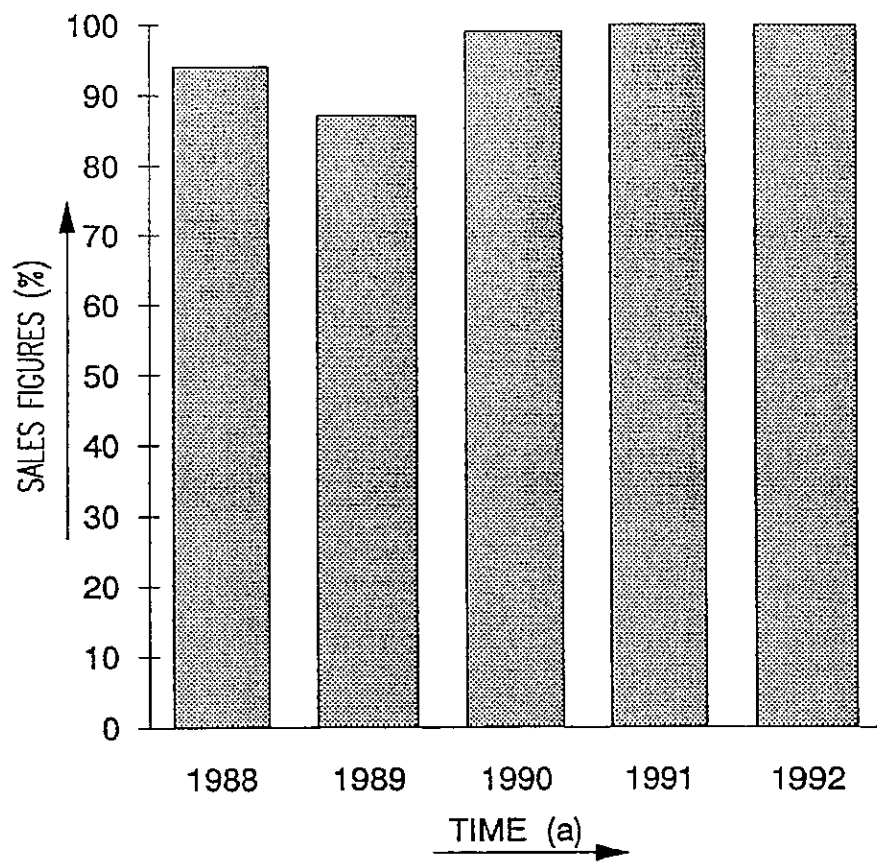


Fig. 4
Sales figures of the product 1988 - 1992

Material	-	+
Frikothem (Al ₂ O ₃)	[Cross-hatched pattern]	[Dotted pattern]
RCH 1000	[Horizontal line pattern]	[Vertical line pattern]
Cast iron (Si)	[Horizontal line pattern]	[Dotted pattern]
Graphite	[Horizontal line pattern]	[Vertical line pattern]
Monel 400	[Horizontal line pattern]	[Dotted pattern]
1. 4571	[Horizontal line pattern]	[Dotted pattern]
1. 4408	[Horizontal line pattern]	[Dotted pattern]
1. 4539	[Horizontal line pattern]	[Dotted pattern]
1. 4529	[Horizontal line pattern]	[Dotted pattern]
2. 4856	[Horizontal line pattern]	[Dotted pattern]

Fig. 5
Experiences gained with materials

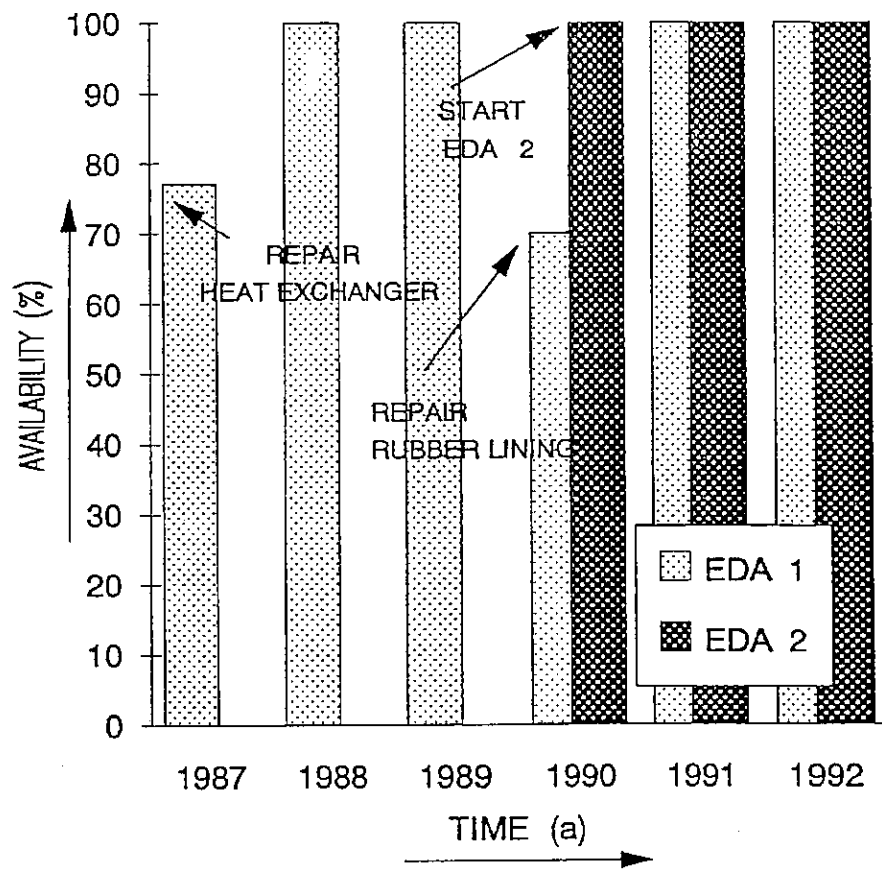


Fig. 6
 Availability of the Herten I and II evaporation plants
 1983 - 1992

SUBSTANCE	1	2	3	4	5	6
NaCl	+	++	++	+	+	++
MgCl ₂				+	++	
CaCl ₂	++		++	++	++	+
Na ₂ SO ₄		++				

- 1 Waste incineration with lime scrubbing
- 2 Waste incineration with soda lye scrubbing
- 3 Waste Incineration with soda lye and lime neutralisation

- 4 Power station with lime scrubbing
- 5 Power station with lime scrubbing
- 6 Power station with lime scrubbing and sodium sulphate treatment

Table 1
Composition of several waste liquors
flue gas purification plants (main components)

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 ₄	<0,01
Cl	47,30
F	<0,01
SO ₄	0,28
NO ₃	0,02

Table 2
Analysis of calcium chloride hydrate