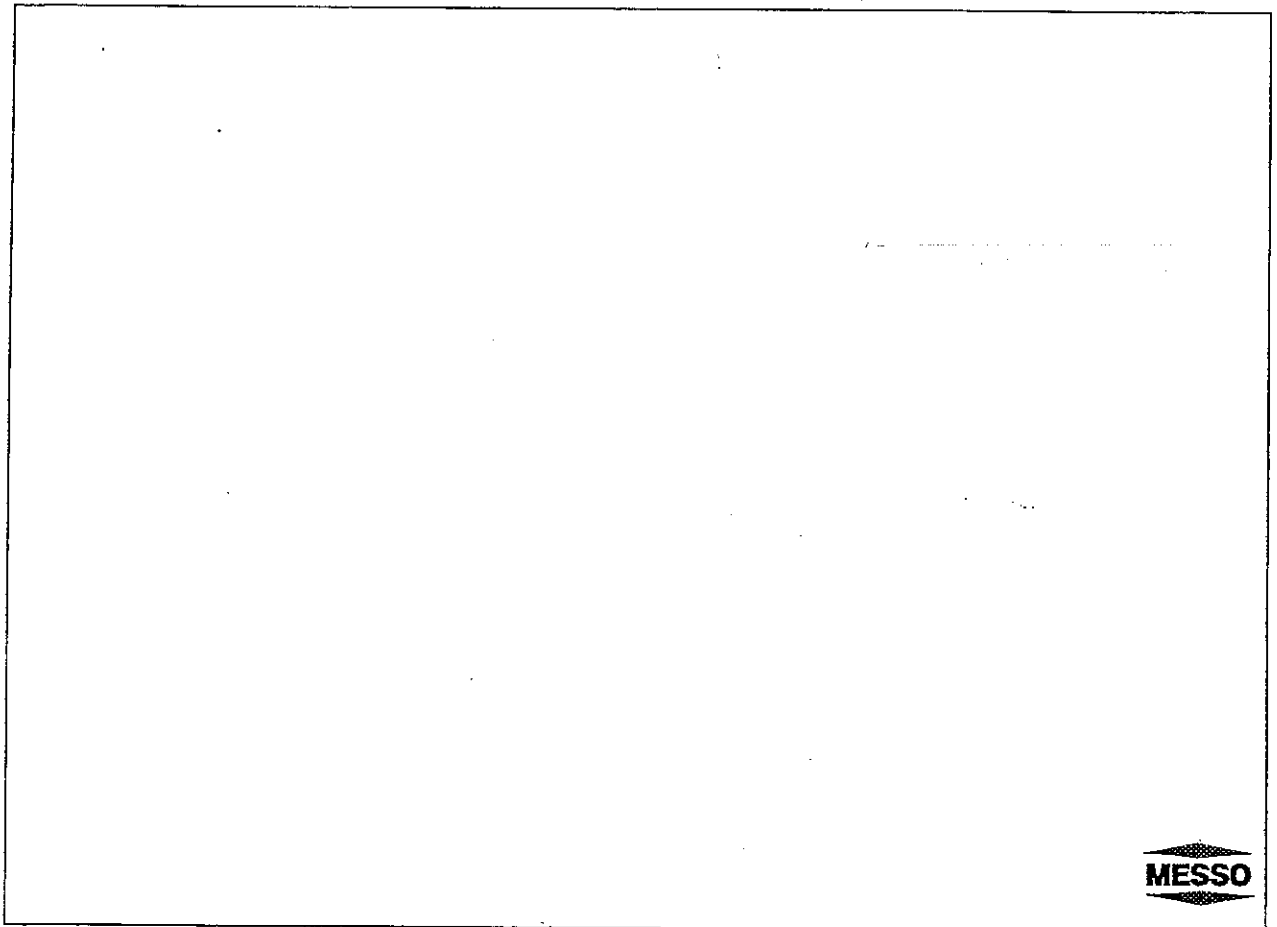


Recycling of Cover Salt in the Secondary Aluminium Industry

Wolfgang Wöhlk, Guido Niederjaufner, Günter Hofmann



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Recycling of Cover Salt in the Secondary Aluminium Industry

W. Wöhlk*, G. Niederjaufner**, G. Hofmann*

*Mannesmann Anlagenbau AG, Messo-Chemietechnik, Düsseldorf, Bundesrepublik Deutschland
**Raffineria Metallì Capra S.P.A., Brescia, Italy

ABSTRACT

The increasing efforts in environmental protection create new targets for the unit operations evaporation and crystallization. Together with problems identical to those from production processes there are new requirements which are often critical for economic solutions. How those problems can be solved is illustrated by the presentation of a new developed process for the preparation of aluminium slags which is one of the today's typical examples. The new development is explained by flow sheets. Special explanations are given for the crystallization step. The process is already tested semi-technically. The installation of a large-scale unit will be started still in 1987.

KEYWORDS

Salt, salt slag, aluminium, secondary aluminium, aluminium-smelter, sodium chloride, potassium chloride, crystallization, evaporation, process, development, environmental protection, mechanical preparation, filtration, degassing.

INTRODUCTION

Per ton of aluminium the secondary aluminium-industry produces an average of 0.5 ton of salt slag. Besides of up to 2/3 salts - mostly NaCl and KCl in a relation of 2/1 - the salt slag contains alumina and rests of metallic aluminium. Up to now most of these salt slags are given to special landfills. In contact with rain or percolating waters a lot of reactions take place and most of them are environmentally not harmless:

The percolating waters become concentrated with salts and by hydrolysis of miscellaneous aluminium compounds large amounts of burnable gases are evolved, some of them very toxic. Up to 2.5 million tons/yr salt slag are given to landfills worldwide (west). Subsequently, abt. 4.3 millions cubic meters percolating waters become saturated with salt and at least 40 millions cubic meters of gases are evolved, mainly hydrogen and methane, but also hydrogen sulphide and phosphine.

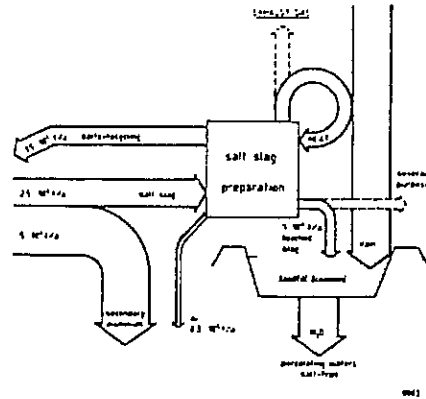


Fig. 1. Salt slag preparation, possible recycling worldwide (west).

Consequently, the perfect process to overcome these environmental problems has to recover salts and metallic aluminium for recycling and to produce an environmentally harmless alumina (Fig. 1) - all that as economically as possible. A process which fulfills these requirements as far as possible was developed and tested at semi-technical scale in co-operation of Mannesmann Anlagenbau AG (Messo-Chemietechnik) and Raffineria Metalli Capra S.P.A.. The large-scale realization is planned to be started this year. Figure 2 shows the block flow diagram of this new process.

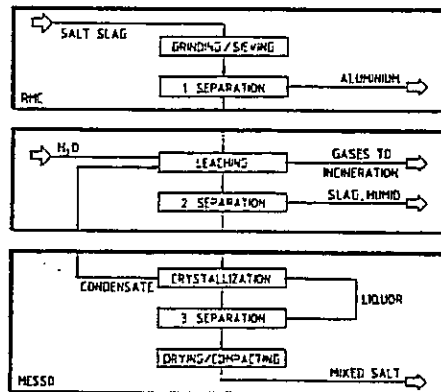


Fig. 2 Block flow diagram.

Within the scope of this paper the crystallization-step is presented as main subject.

THE PROCESS

Mechanical preparation (Fig. 3)

First of all the slag ingots are treated with a hammer-mill. By this, the metallic aluminium is merely deformed and can be separated. After several fractionations and crushings 90 % (wt.) aluminium in the fraction larger than 20 mm, 70 - 80 % (wt.) aluminium between 20 and 1 mm and a salt slag in particle sizes below 1 mm are finally recovered. The aluminium is recycled to the smelters, whereas the salt slag is given to the leaching process. This part of the preparation is already in operation at large-scale.

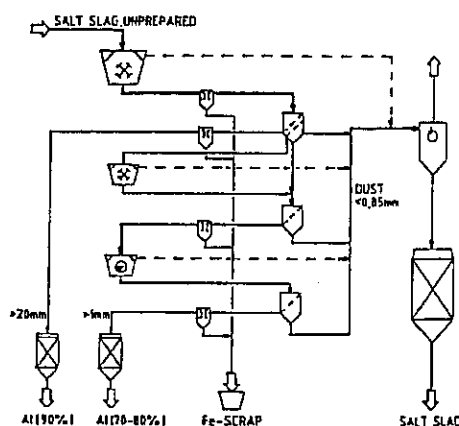


Fig. 3 Flow sheet: mech. preparation

Leaching

Four objectives should be obtained with the leaching process:

1. The salt content of the slag has to be dissolved completely.
2. The solution should be concentrated as far as possible.
3. To achieve a negligible gas production by the later residue, sufficient time should be given to the degassing reaction which starts, getting into contact with water. Toxic gases should be removed completely.
4. The residue (alumina) has to be separated completely from the salt solution. After washing its chloride content should be less than 0.5 % (wt.).

Dissolution, degassing

Typical plots for the degassing reaction during leaching are shown in Fig. 4. The results are taken from different samples. By rising temperature the specific gas production is increased. At low temperatures the degassing needs much more time. Cooling down after leaching, e.g. at a temperature of 86° C, the further reaction becomes again negligible, if the time for leaching has been long enough to finish the first heavy reactions. Figure 5 demonstrates the gas composition as a function of time for a leaching temperature of

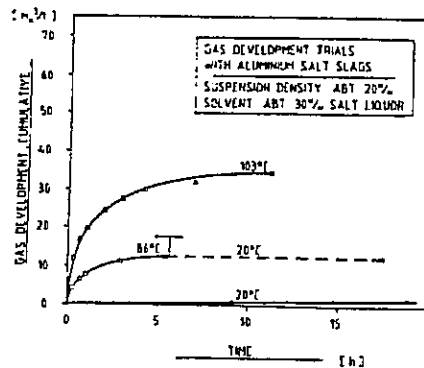


Fig. 4 Typical gas developments.

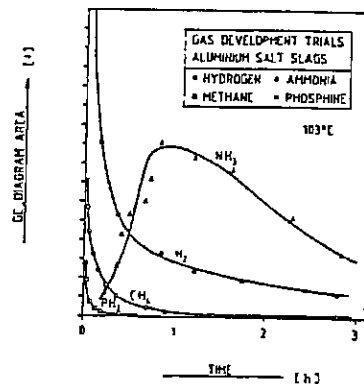


Fig. 5 Gas composition as function of time.

103° C. The production of phosphine is finished already after half an hour of leaching, i.e. its concentration becomes lower than detectable. Also the methane concentration slopes down quickly, whereas hydrogen after an explosion-like reaction during the first minutes comes down moderately. The concentration of ammonia is low at the beginning, due to its large solubility in water.

From these experiments the following results could be taken:

1. Leaching at temperatures near to the atmospheric boiling point leads to a fast and effective degassing reaction. First of all, the evolution of toxic gases can be completed within a short time.
2. The time necessary for the degassing reaction always will exceed the time for dissolving the salt content. The layout for the leaching station (Fig.6), therefore, is not directed to the dissolving rates.

The leaching at high temperatures is mainly supported by the hydrolysis reactions, which are exothermic. The small rest of heat is taken from the incineration unit, which is processed to bring out the waste gases.

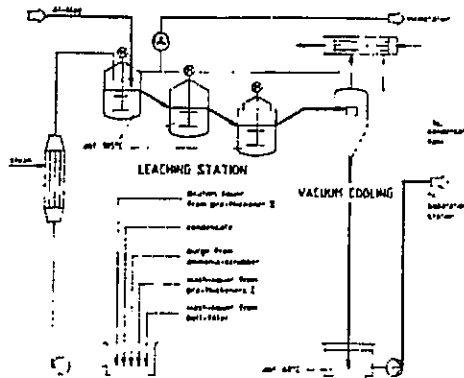


Fig. 6 Flow sheet: leaching.

Separation

The desired low chloride content in the treated residue is achieved by combination of pre-thickeners with a vacuum belt-filtration. By pre-thickening the solution overflow becomes almost completely free of suspended solids, whereas the belt filtration is used to achieve residues with a low chloride content by counter-current washing. Prior to separation the hot suspension is vacuum-cooled first. Pre-thickening can be done in two steps (Fig. 7). By a group of rake-classifiers it is possible to catch the fast settling fraction first. This coarse fraction contains nearly all metallic aluminium which still remains after mechanical preparation. The overflow is given to the pre-thickener together with a flocculant. The underflow of the pre-thickener is separated on the vacuum belt-filter, the filtrate is recycled and the filter-cake is washed counter-current wise. Wash waters are recycled to the leaching station. The clear-liquor overflow of the pre-

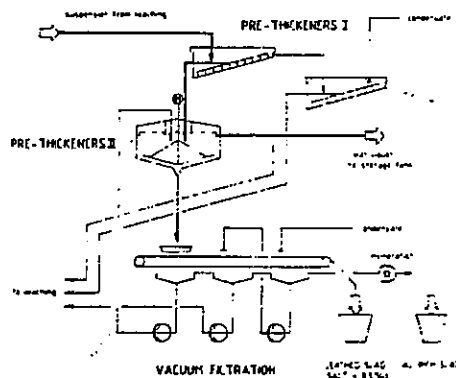


Fig. 7 Flow sheet: separation.

However, slag compositions often will be constant so far to chose the direct crystallization of a mixed salt quality. The mixed salt quality then, of course, is connected with the present salt slag composition. Light fluctuations in slag compositions are compensated by the existing buffers for process solutions (pre-thickeners, tanks, crystallizer). Fluctuations in mixed salt compositions are also possible if there are incrustations in the crystallizer unit. Necessary wash-outs again take influence. For that reason (beside others) plant details should be constructed such that incrustations are excluded farrest possible.

In our present project the crystallization of mixed salt is possible. Generally an evaporative crystallization like this is realized as a multi-stage unit to reduce energy consumption if steam is used. For certain relations of specific costs the electrically operated mechanical vapor compression can be the more economic solution. MVC-units are single-staged, therefore more simple in respect to crystallizer operation. In our present project the MVC could be chosen.

Also the second condition, i.e. the special particle size, made certain difficulties. Figure 9 shows the three basic types of industrial crystallizers usable for evaporative crystallization (Wöhlk, 1985). Their applicability for this purpose is discussed below:

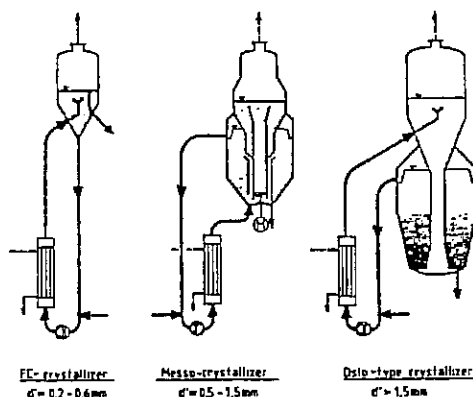


Fig. 9 Basic types of industrial crystallizers.

Every crystallization can be seen as a competition between crystal growth and nucleation rate. To achieve large crystals, low nucleation rates are necessary. Nucleation can be minimized by a lot of factors, e.g. by appropriate selection of circulation pumps or by crystallization in a fluidized-bed, in which the crystals are not in contact with pumps. Examples are the Oslo-type crystallizer as a fluidized-bed crystallizer, wherein nucleation happens only by crystal/crystal-impacts and the Messo-type crystallizer with a special impeller pump. The latter achieves its nearly as low nucleation rates as in Oslo-type crystallizers by the combination of low impeller tip-speeds together with the reduction of dissipated energy, compared with normal FC-crystallizers. In FC-type crystallizers the dissipated energy and therefore the nucleation rate are both much larger, because the circulation pump has to operate against a much larger pressure head. Additionally the impeller tip-speeds of pumps in external positions are higher.

thickener is a more or less pure solution of sodium and potassium chloride. All other substances together are not more than 1 g/l. By a small purge from crystallization back to leaching an up-grading of these impurities and influences to crystallization can be avoided easily.

Crystallization

Re-using of the salt-mixture NaCl-KCl as a cover salt in aluminium smelters two conditions are of importance:

1. The melting point of the slag depends on the chemical composition of the cover salt:

A mixed salt with abt. 65 % (wt.) NaCl and 35 % (wt.) KCl is preferred.

2. The particle-size distribution has to be suitable for furnace operation.

The allround recovery method to get certain salt compositions starting from various slag compositions is the separate crystallization followed by a backmixing of both salts to the salt composition desired. The appropriate crystallization process is based on the phase system NaCl-KCl-H₂O (Seidell, 1965; Fig. 8). Above the polytherme NaCl can be crystallized, below KCl. Point 2 (NaCl/KCl abt. 2) is a typical point for the leaching liquors from salt slags. Starting evaporation at higher temperatures (here 110° C) those solution will only be concentrated up to point 3, i.e. saturation concentration is reached. Then, NaCl is crystallized, following the isotherme for 110° C. At the same time KCl is only concentrated. In point 4 NaCl can be separated. By adding some water after separation the polytherme is crossed again. Now KCl can be crystallized, and separated (point 2). By backmixing both salts any mixed salt composition can be prepared that way.

A disadvantage of this separate crystallization is the high investment due to double equipment, namely crystallizers, pumps, centrifuges and driers and by the heat-recovery system necessary to prevent too high energy consumptions. Generally, this investment cannot be financed by increases of wealth creation.

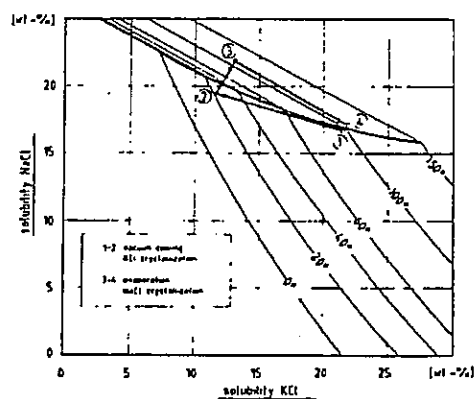


Fig. 8 Separate crystallization of KCl and NaCl

While the reduction of secondary nucleation is essential to achieve large crystals, the controlled fines dissolving is of similar importance. Fines dissolving is possible by adding water (solvent) or by increasing temperature, generally. Water (solvent) on principle is always usable, but a fines dissolving in this case is achievable only by an uneconomical high addition. Uneconomical, because water has to be evaporated again. On the other hand a fines dissolving by increase of temperature in heat exchangers is always free of charge in evaporative crystallization. So it is obvious to use this effect. Figure 10, which shows a sector of the phase system, explains what happens with fines dissolving in this case. The heat is brought into a solution which still contains fines of both salts. The solution is saturated (point 1). While heated up, the concentration point follows the polytherme until point 2 and creates dissolving capacity only for KCl. As long as KCl-crystals are present, NaCl becomes supersaturated.

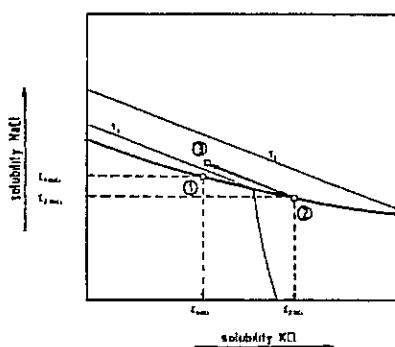


Fig. 10 Fines dissolving.

This supersaturation may cause incrustations, e.g. in heat exchanger tubes and on crystallizer baffles if it is not taken into account. Instead of a certain reduction of nuclei and fines the result of this fines dissolving could be an increase in incrustation behaviour. For that reason it was decided to give up the direct production of large crystals. The FC-crystallizer was chosen (see Fig. 9). This decision only could be made after proving the possibility of compacting the produced mixed salt with a good commercial efficiency. Briquetting machines brought best results with breaking strength of the briquettes, which allow storing in silos without problems. For the crystallization step, therefore, it was decided to take the following conception (Fig. 11):

The single-staged FC-crystallizer is fed from the clear-liquor storage tank and operated with mechanical vapor compression. Before feeding the crystallizer the rest of ammonia first is stripped off with steam. The ammonia-containing vapors are mixed with the main stream from the crystallizer and then treated with sulphuric acid-solution to wash out ammonia.

The washed vapors enter the mechanical vapor compressor. After compressing they are saturated by adding condensate and then given to the heat exchanger to be condensed and to maintain evaporation.

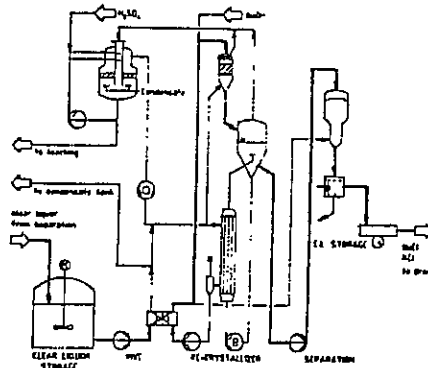


Fig. 11 Flow sheet: crystallization, separation.

The produced suspension first is given to a pre-thickener with washing-device. Hot liquor is changed against the cooler feed solution. So the centrifugation takes place under good conditions. The separated crystals are proceeded to the drier, compacted and stored.

ACTUAL FIGURES TO ECONOMY

For information see Fig. 12.

The figures are based on a plant for a slag-capacity of 65,000 t/yr. The point "process utilities" (26 DM/t) includes the costs for depositing on landfills (18 DM/t slag-input). In case of recycling the specific costs would decrease to DM 135.

COSTS	DM/TON _{SLAG}
LABOUR	28
PROCESS UTILITIES (WATER, CHEMICALS, STEAM, WASTE DISPOSAL)	26
EL. ENERGY	37
MAINTENANCE SUPPLIES	10
OVERALL PLANT ADMINISTRATION	4
DEPRECIATION	43
INSURANCES, TAXES	5
	753
WEALTH CREATION	
ALUMINIUM	80
AL-RICH RESIDUE	1
MIXED SALT	75
RESIDUE (HUMIDITY 40%), SAVINGS	47
	197

Fig. 12 Economics.

The specific wealth creation possible by the Al-rich residues is not known up to now. The process is still under development. With 25 to 30 % (wt.) metallic aluminium and 3,000 t/yr the specific value is approximately 18 DM/t slag-input and, therefore, not negligible.

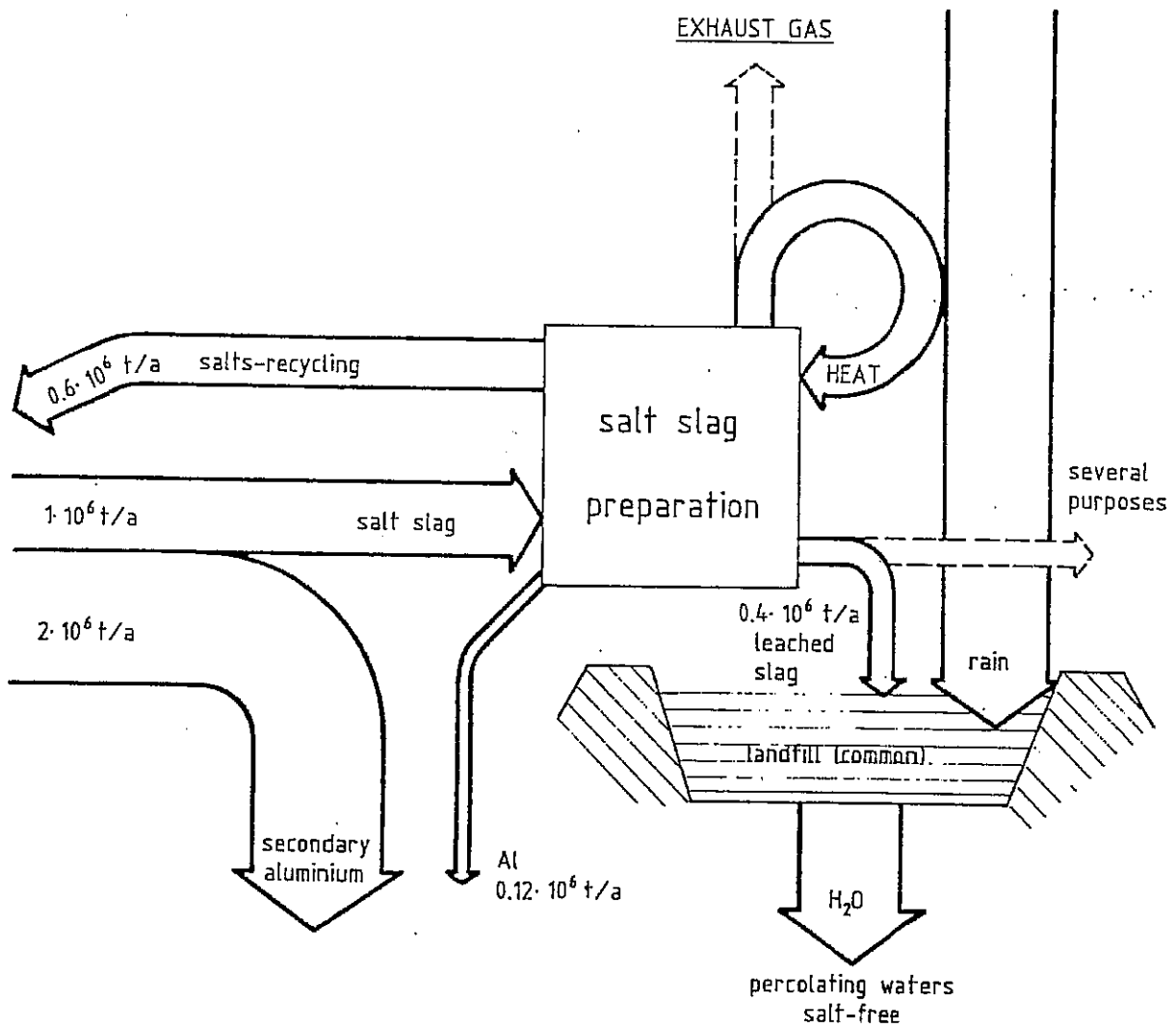
Wealth creation is considered to be available also for the washed residue. It is calculated as the cost reduction which is possible as difference between the specific cost for the disposal of the original (80 DM/t) and the washed slag (30 DM/t).

As it results from this listing, the preparation of aluminium slags has more than environmental advantages. A further rise in depositing costs, which is expectable, will increase the necessity for recycling also by financial reasons.

Consequently, Raffineria Metalli Capra S.P.A. will complete their mechanical slag preparation by leaching and crystallization this year.

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Wöhlk, W., and G. Hofmann (1985). Chemie-Ingenieur-Technik, 4, 352-355.

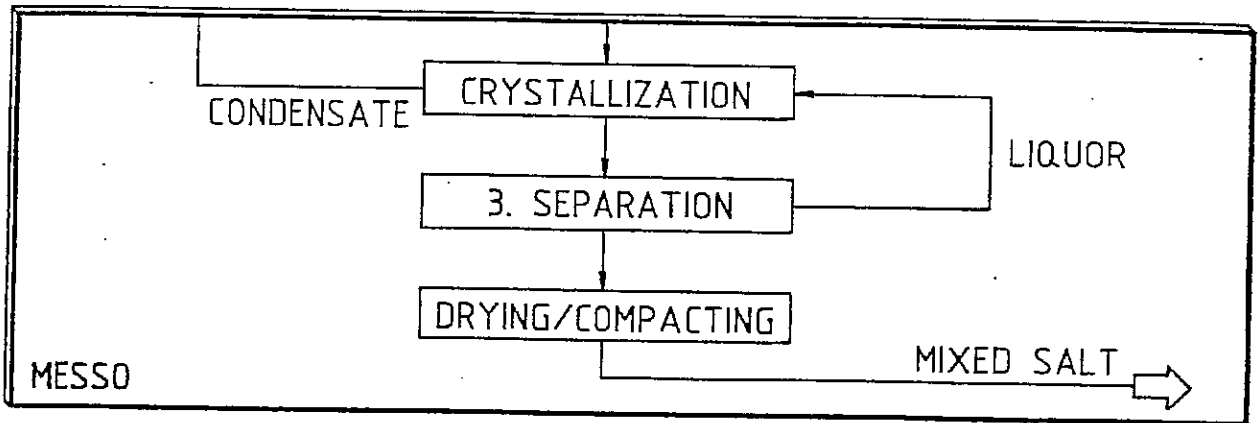
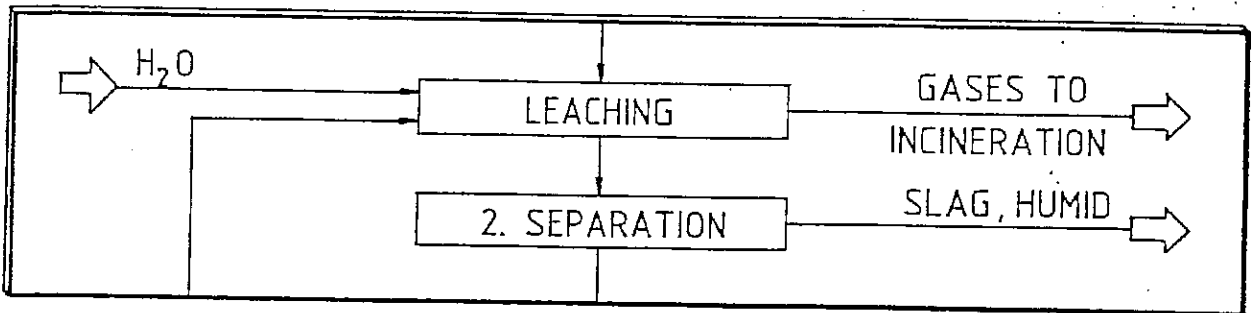
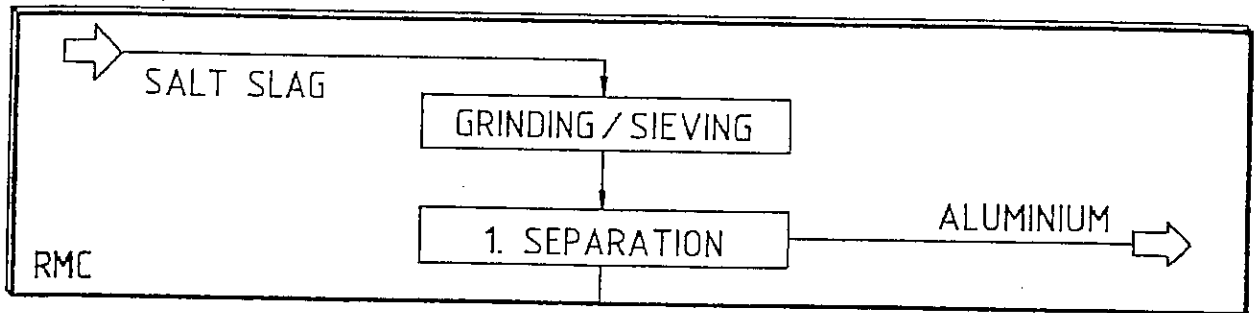


1983



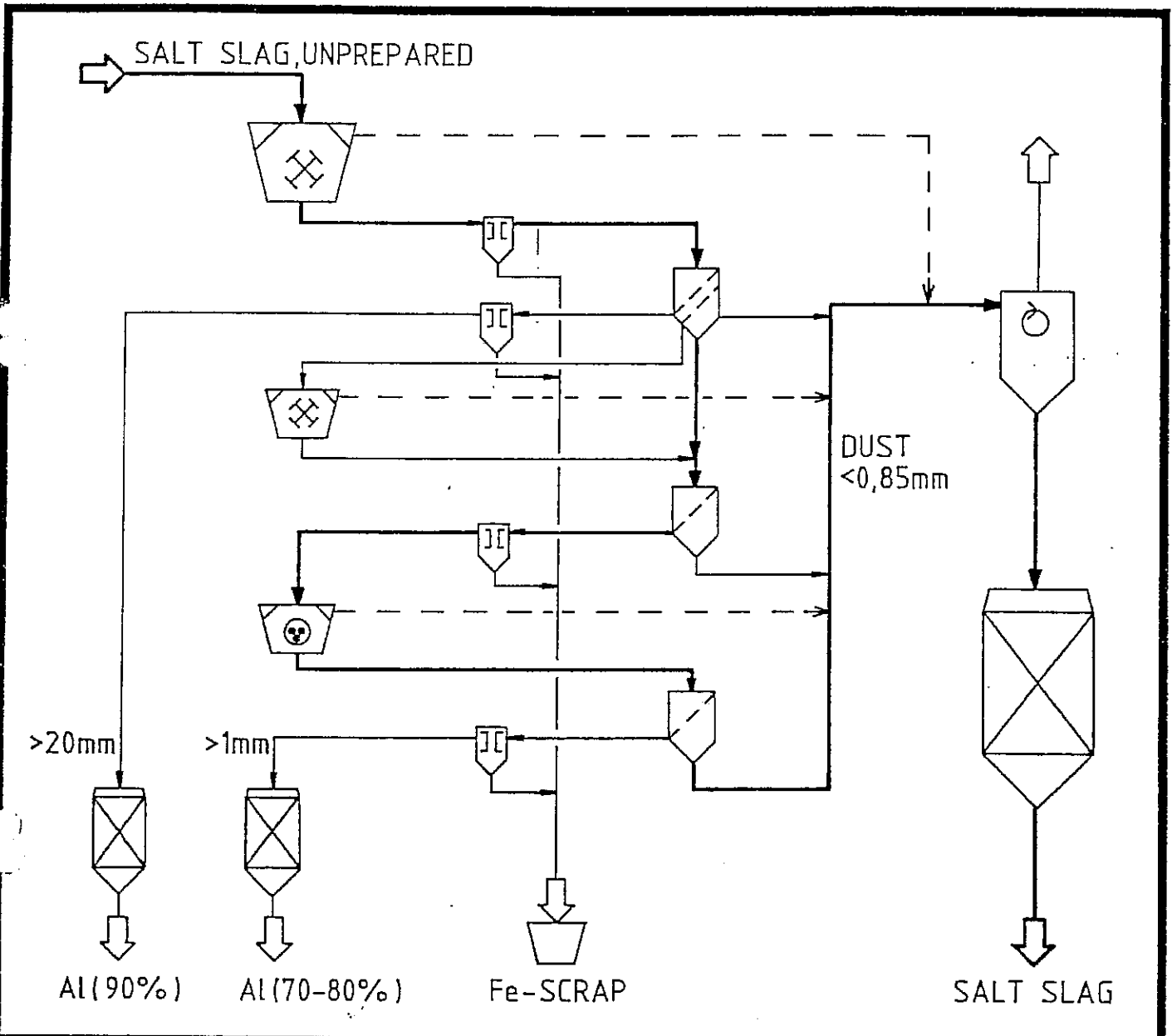
SECONDARY ALUMINIUM INDUSTRY (ROTARY FURNACE)
 WORLDWIDE (WEST)
 PRODUCTION WITHOUT POLLUTION

①



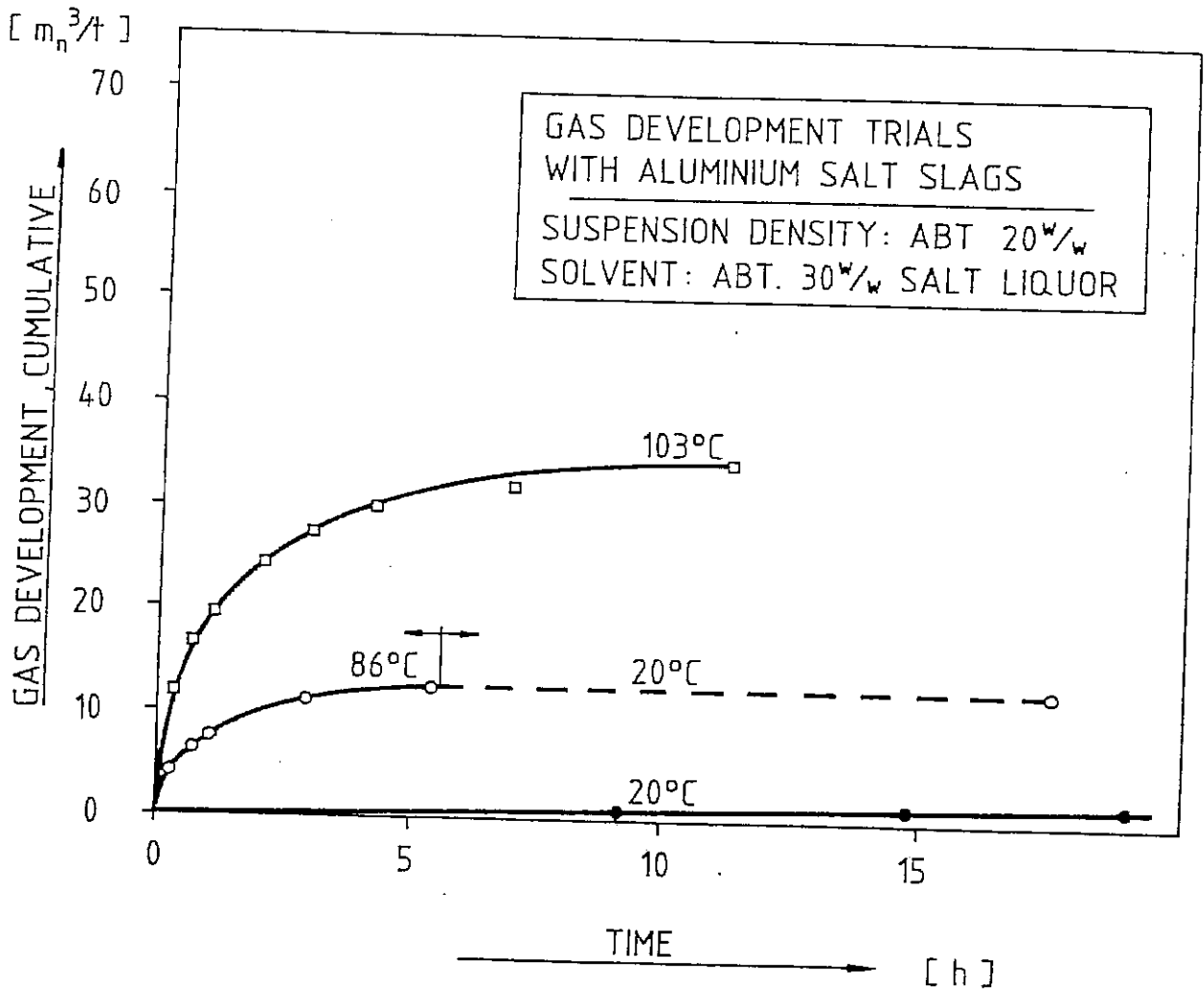
BLOCK FLOW DIAGRAM

2



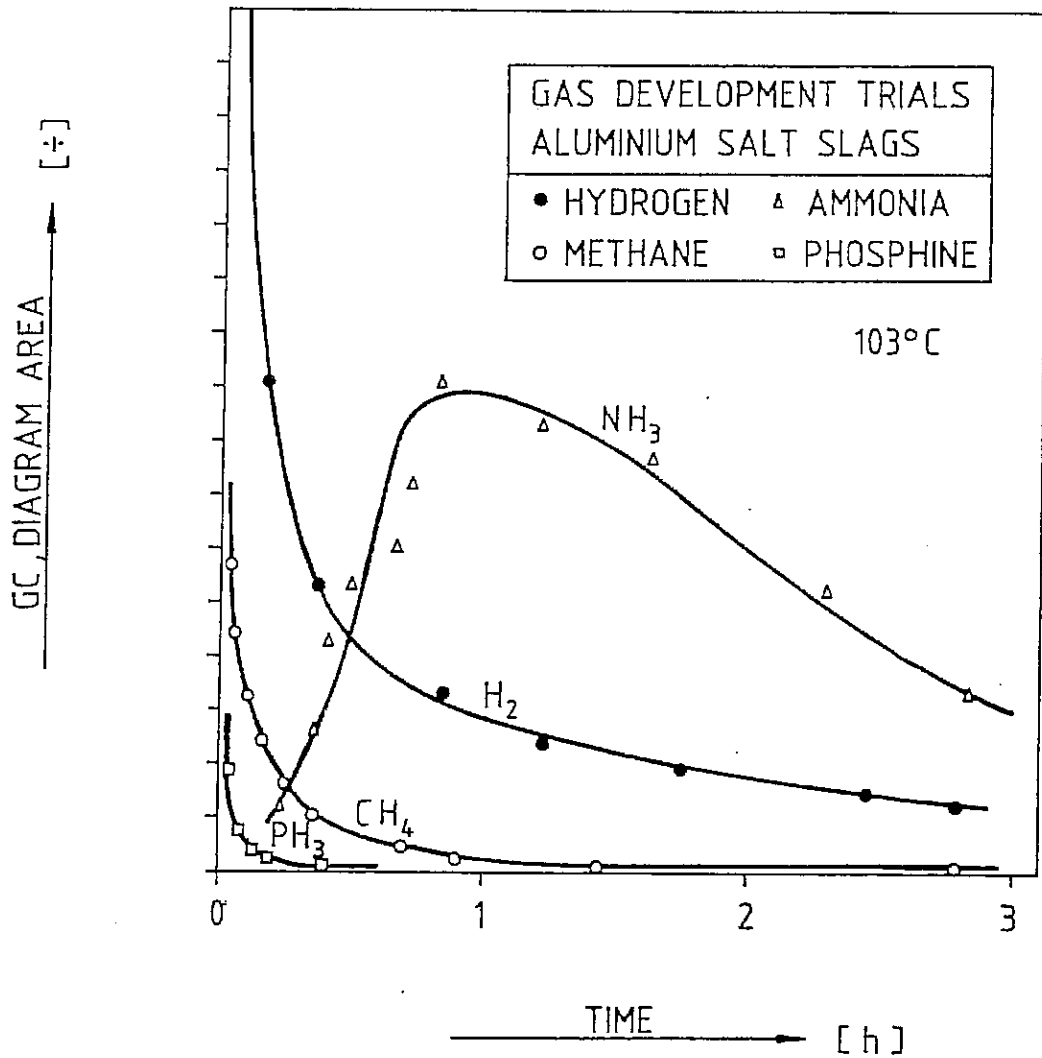
FLOW SHEET : MECH. PREPARATION

3



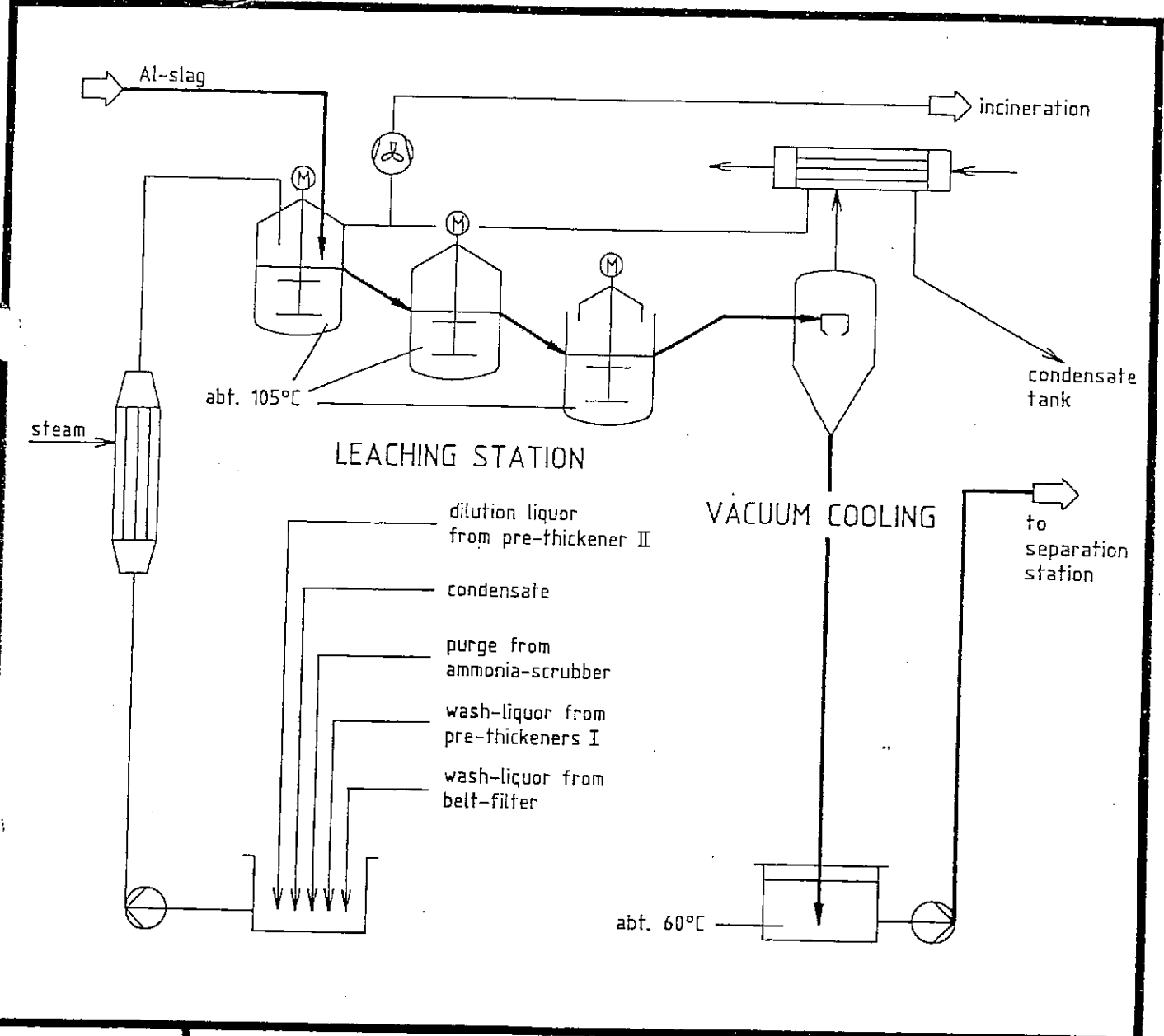
TYPICAL GAS DEVELOPMENT GRAPHS
AS A FUNCTION OF TEMPERATURE

4



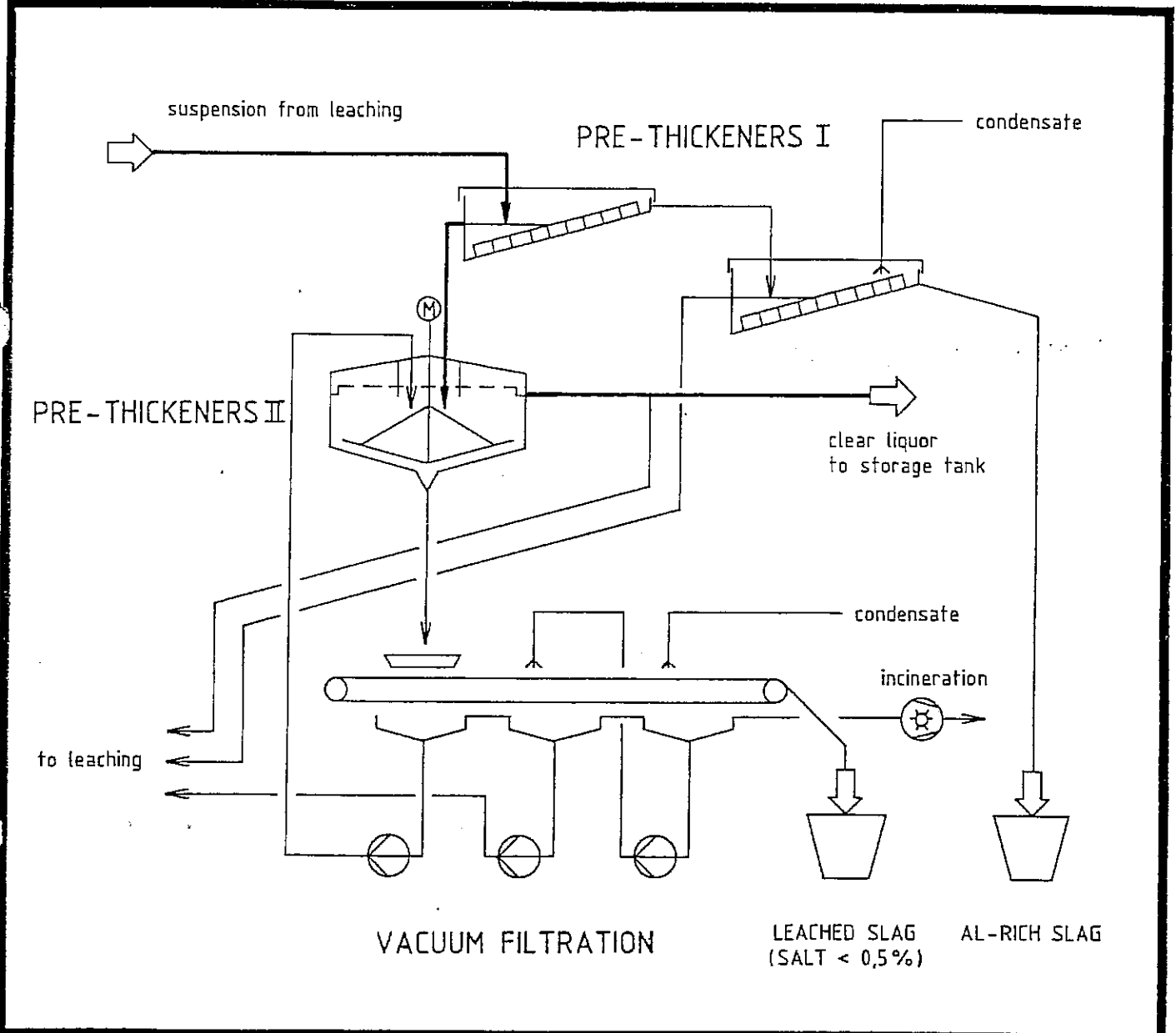
TYPICAL BEHAVIOUR GAS COMPOSITION
(GC - GRAPHS)

5



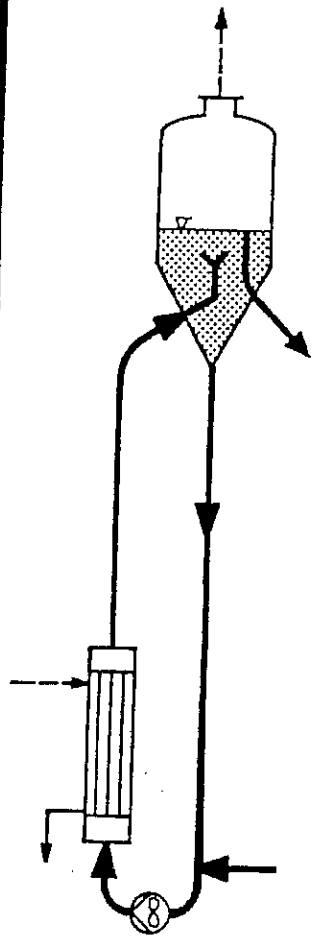
FLWSHEET: LEACHING

6

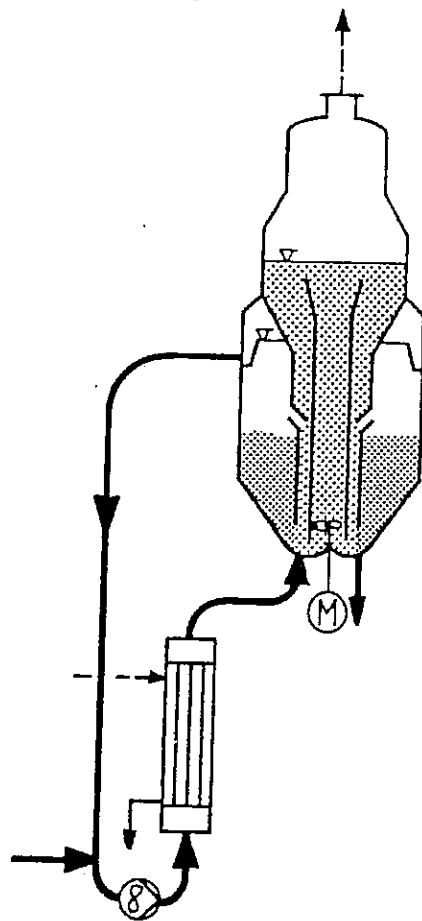


FLWSHEET: SEPARATION

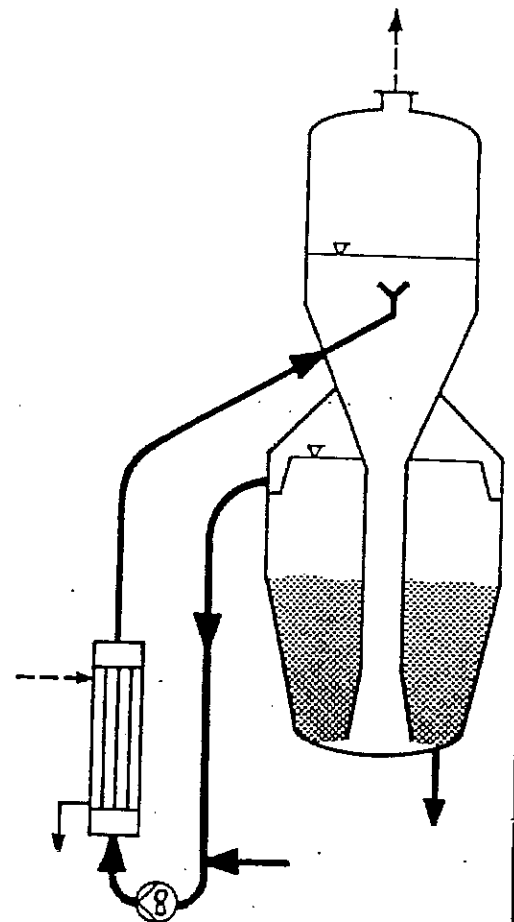
7



FC-crystallizer
 $d' \approx 0,2 - 0,6 \text{ mm}$



Messo-crystallizer
 $d' \approx 0,5 - 1,5 \text{ mm}$

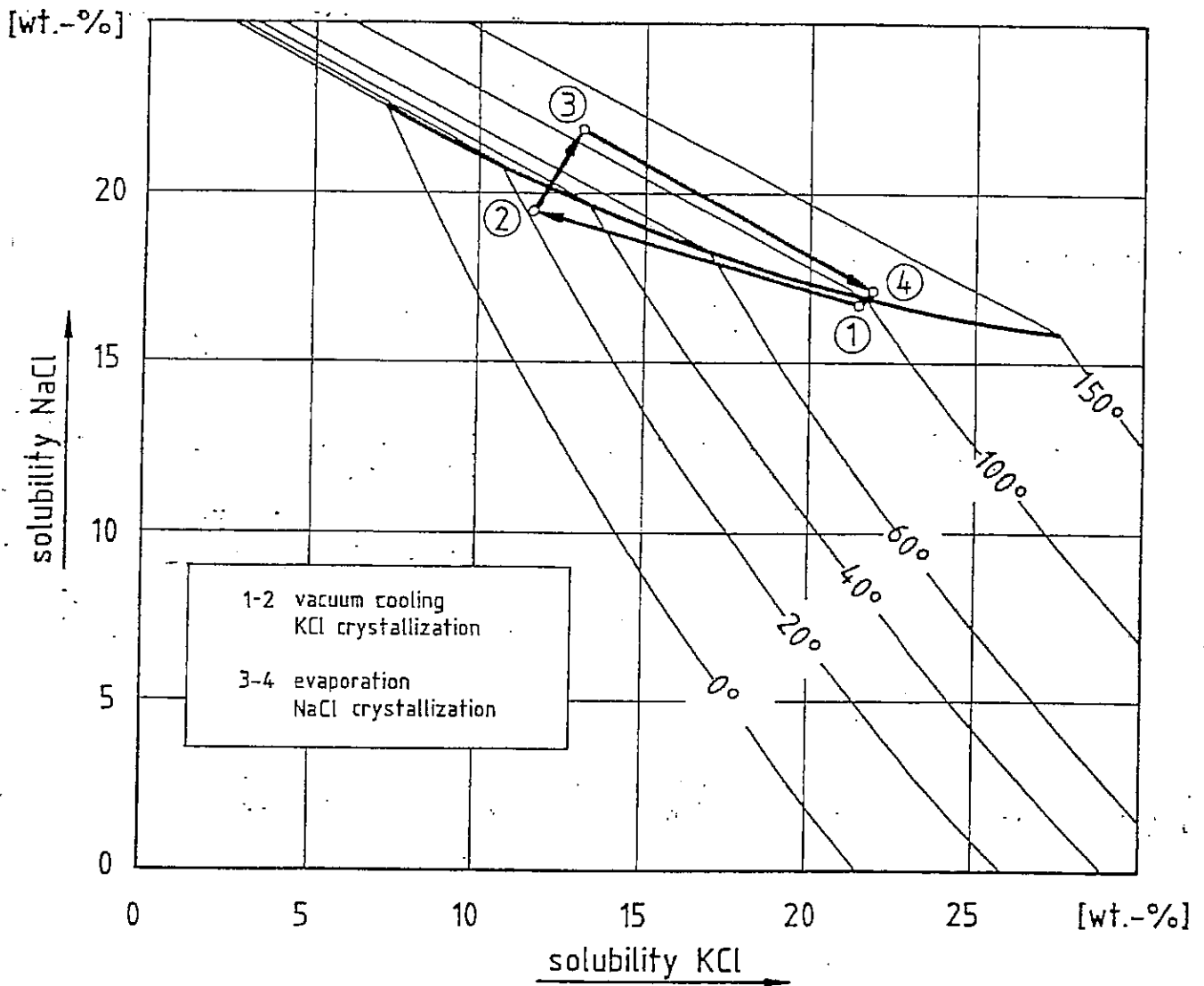


Oslo-type crystallizer
 $d' > 1,5 \text{ mm}$



BASIC TYPES
 OF INDUSTRIAL CRYSTALLIZERS



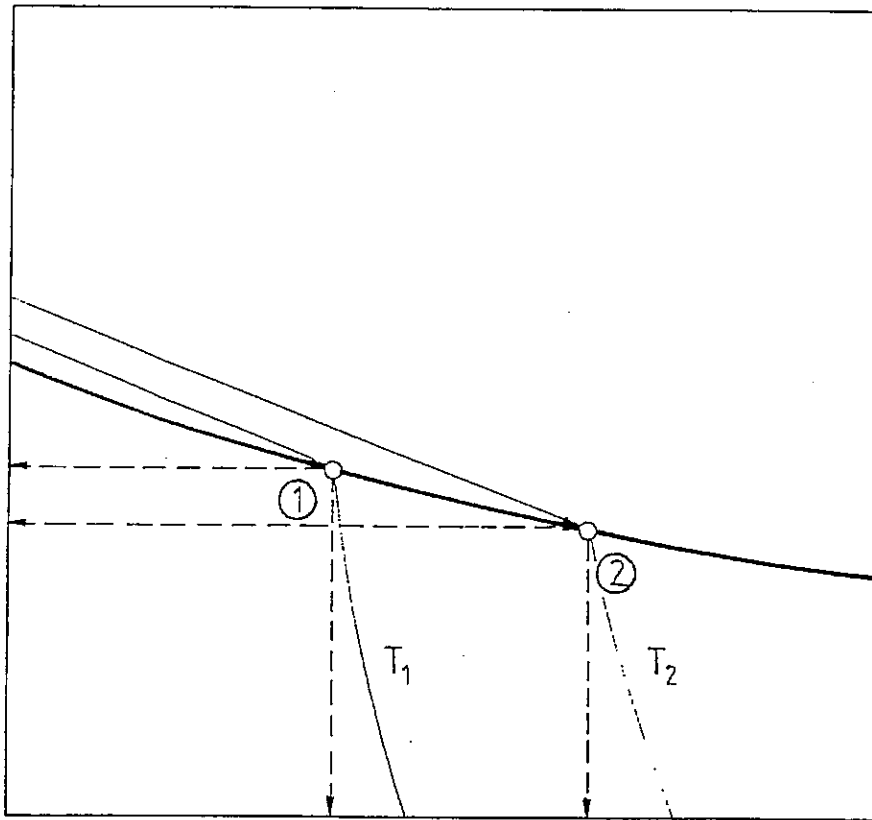


SEPARATE CRYSTALLIZATION OF KCl. AND NaCl

9

solubility NaCl

$c_{1,NaCl}$
 $c_{2,NaCl}$



$c_{1,KCl}$

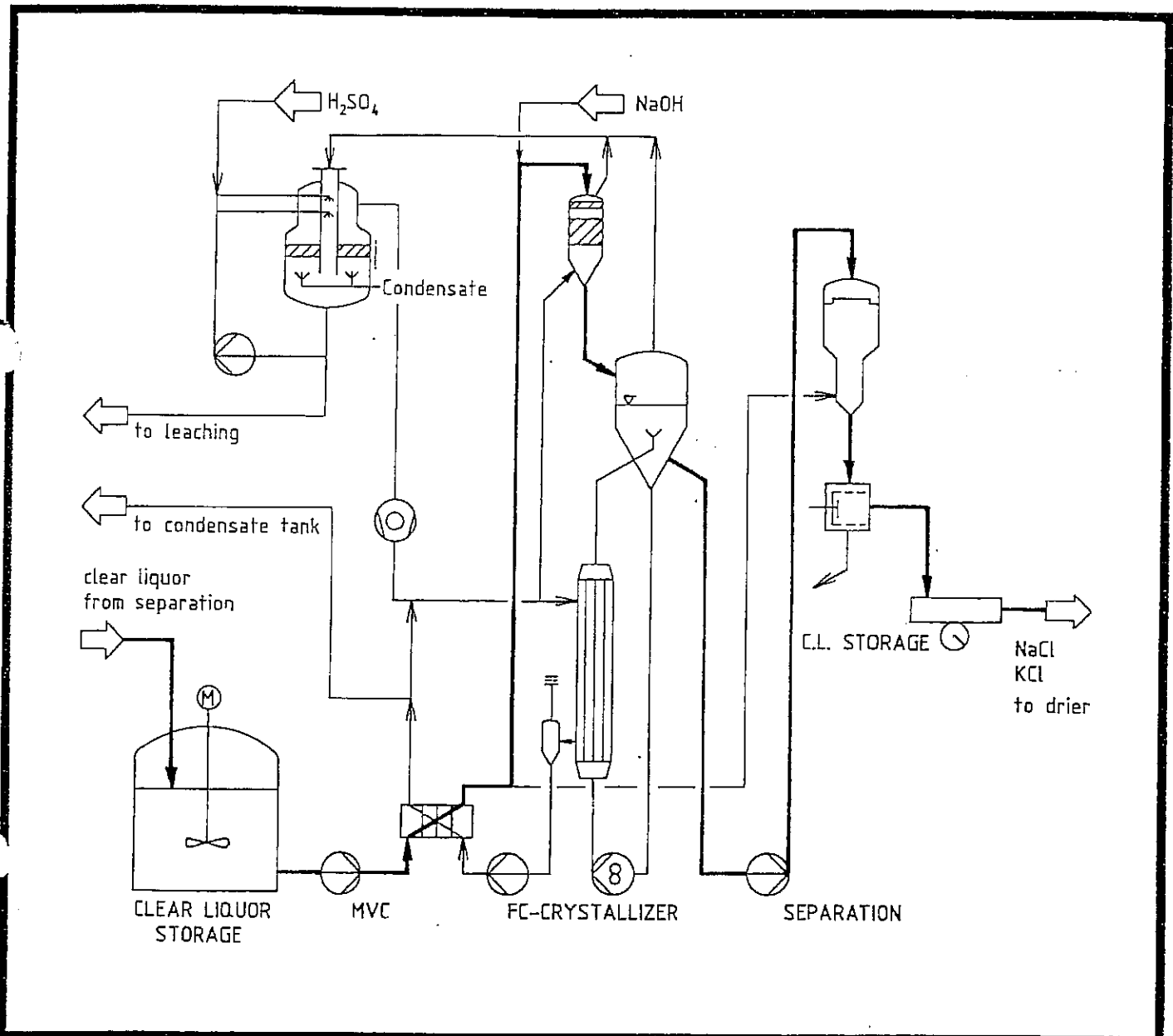
$c_{2,KCl}$

solubility KCl

MESSO

HEATING UP IN PRESENCE OF BOTH
CRYSTALLIZATES

10



FLWSHEET: CRYSTALLIZATION, SEPARATION

11

COSTS	DM/TON _{SLAG}
LABOUR	28
PROCESS UTILITIES (WATER, CHEMICALS, STEAM, WASTE DISPOSAL)	26
EL. ENERGY	37
MAINTENANCE SUPPLIES	10
OVERALL PLANT ADMINISTRATION	4
DEPRECIATION	43
INSURANCES, TAXES	5
	<u>153</u>
WEALTH CREATION	
ALUMINIUM	50
AL-RICH RESIDUE	?
MIXED SALT	71
RESIDUE (HUMIDITY 40%), SAVINGS:	61
	<u>182</u>



ECONOMIC SITUATION (ABT. 65.000 TONS/YR)

12