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MASS BALANCE OF HEAVY METAL IONS IN HEMIHYDRATE PHOSPHORIC ACID PROCESSES

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ABSTRACT

A mass balance computer program, which calculates the concentrations of some macro and micro components in the process streams of a Norsk Hydro hemihydrate (HH) and hemidihydrate (HDH) phosphoric acid process, has been developed. The program demonstrates the reduced disposal of impurities and phosphate via the calcium sulfate slurry in a HDH process compared to a HH process, as well as the higher disposal of impurities in case of lower wash, filter or recrystallization efficiency or anhydrite formation. Which step in the process can best be optimized for achieving the best process performance can be sorted out using the program.

INTRODUCTION

Calcium sulfate, which is formed during phosphoric acid production, is usually disposed as an unwanted byproduct and should thus have an acceptable purity for environmental reasons. The quality of the produced phosphoric acid also largely depends on the concentrations of minor impurities. Therefore control of these concentrations in the calcium sulfate as well as in the phosphoric acid is a stringent demand. Control and optimization of the impurity concentrations in the several process streams require a detailed mass balance and the knowledge of parameters such as the composition of the ore and the distribution coefficients of impurities in the respective calcium sulfate hydrates. A distribution coefficient K is defined as the concentration of the impurity in the particular crystals divided by its concentration of the mother liquor, thus $K = [\text{impurity}]_{\text{crystal}} / [\text{impurity}]_{\text{liquor}}$. Its value is influenced by a large number of parameters like the prevailing calcium/sulfate concentration ratio or stoichiometry, the supersaturation and the presence of other impurities. From literature [1,2] the K values are known for a large number of ions in the three calcium sulfate phases and the most accurate distribution coefficients are of course those determined in the same type of process under similar process conditions with the same ore.

With these K values and a computer model of the mass balance the impurity concentrations in the process streams can be calculated. In this paper the effects of the wash, filter, digestion and recrystallization efficiencies and of the anhydrite formation in the Norsk Hydro HDH process are evaluated while also the HDH process is compared with the HH process. Finally the relation between the K values in the HH and DH and the resulting impurity concentrations in the disposed calcium sulfate will be demonstrated.

DESCRIPTION OF THE COMPUTER MODEL

In a HDH process three process steps, can be distinguished [3]:
a digestion step (1), a HH crystallization step (2) and a HH into DH recrystallization step (3):

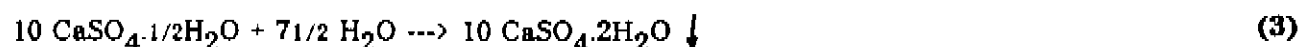
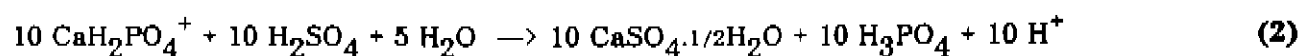
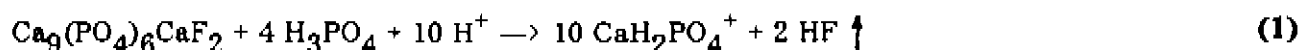


Figure 1 and 2 show the process schemes for a Norsk Hydro HDH and a Norsk Hydro HH process. The digestion almost exclusively takes place in tank A, while the HH crystallization occurs mainly in tank B (70 % compared to 30 % in A). Because of a large slurry recycle flow (recycle ratio of 8), no distinction can be made between HH crystals formed in tank A or B. In the model A and B are therefore represented by a single reactor. The recrystallization of HH into DH in the HDH process takes place in tank C, which in practice consists of 1 or 2 reactors in series.

The process conditions of the HH and HDH process are given in table 1.

TABLE 1 - THE APPROXIMATE PROCESS CONDITIONS IN A HH AND A HDH PROCESS

	HH section (HH or HDH)	DH section (HDH)
total residence time in section	5 hrs	5 hrs
solid content	33 w%	40 w%
temperature	95 °C	60 °C
H ₃ PO ₄ concentration	58 w% (Φ_7)	8 w% (Φ_{19})
H ₂ SO ₄ concentration	2 w% (Φ_7)	5 w% (Φ_{19})

The model consists of detailed mass balances of both the macro components like P, Ca, S and the micro components over the reactors and the several filter sections. The equations are solved with the software package MathCadTM (see appendix 1).

In the calculation of the mass balances the following assumptions are made for the standard case:

- i) The reactors are considered to be continuous stirred tank reactors.
- ii) All reactions occur exclusively in the reactors and not in the pipes or filter sections.
- iii) The reaction kinetics of the digestion and (re)crystallization processes are not rate determining.
- iv) The impurities enter the plant only with the ore. Losses via off gases are neglected.
- v) The concentrations of the micro components are so low (ppm level), that they do not influence the concentrations of the macro components (% level). This implies that the distribution coefficients of the micro components and their concentrations can be varied, without influencing the mass balance of the other components.
- vi) The liquor, attached to this filter cake has the same composition as the filtrate. Deviations from this assumption are taken into account as a wash efficiency.

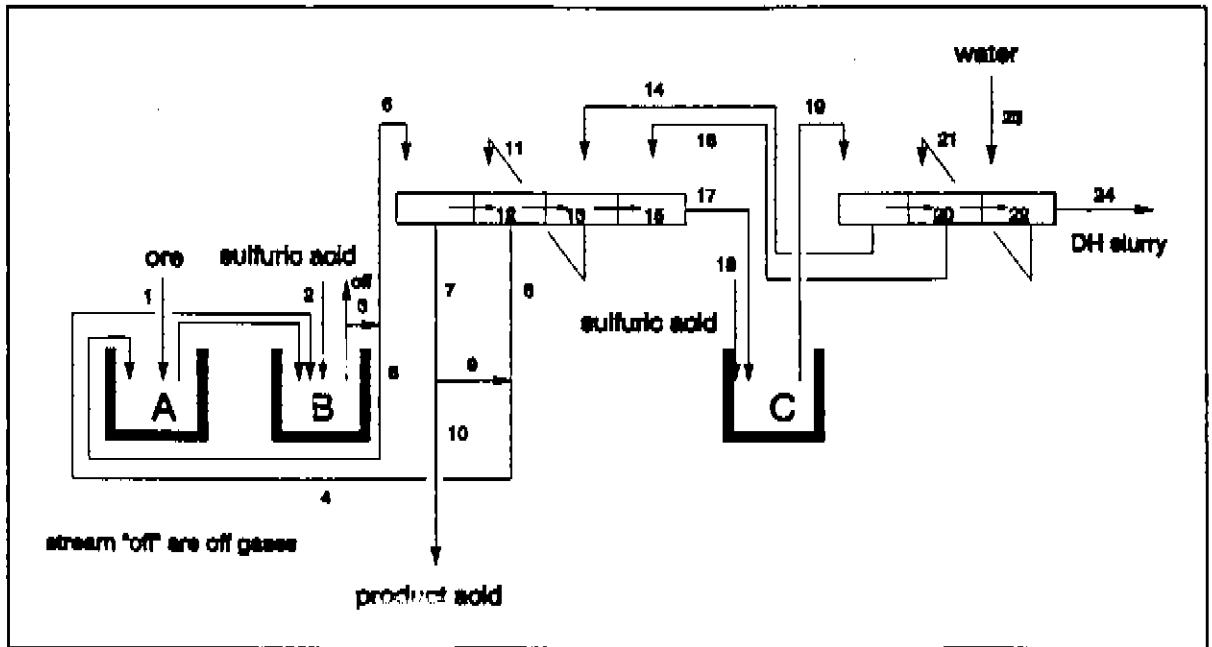


Figure 1 The Norsk Hydro HDH process of Hydro Agri Rotterdam B.V..

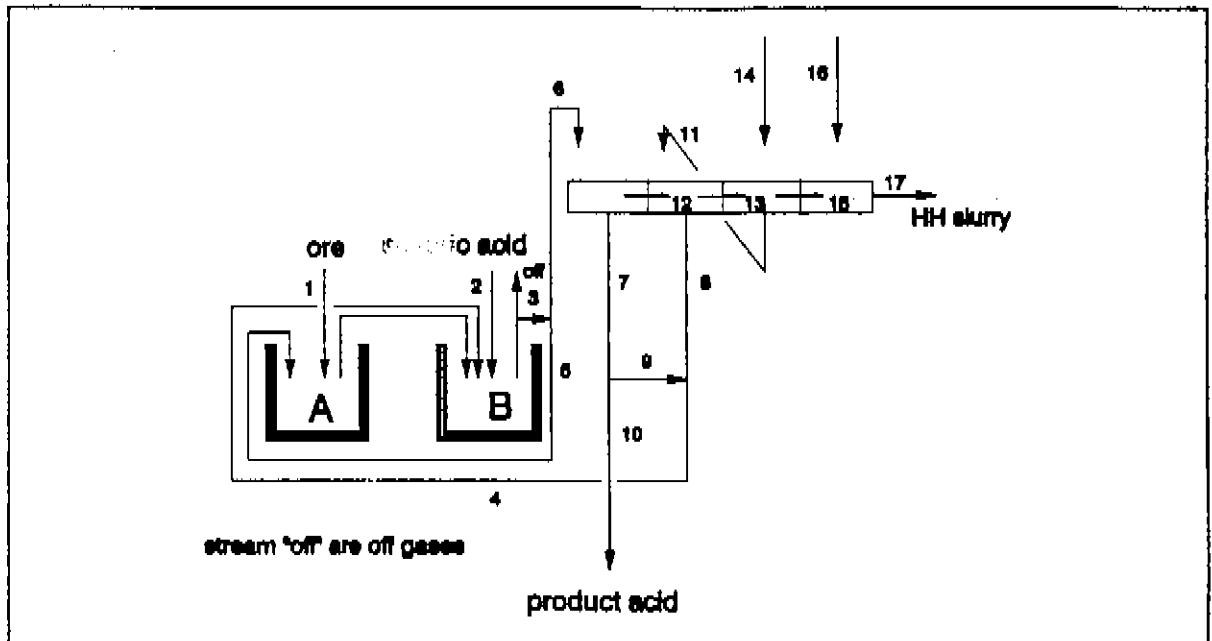


Figure 2 A Norsk Hydro HH process.

The computer model requires several input parameters. In case of the HDH process configuration the input parameters are the total mass flows (\dot{m}_{tot}) of the streams 1, 2, 6, 9, 10, 11, 14, 16, 19, 21 and 23 and the HH and DH mass flows. Except for the streams 9, 11 and 21 all these streams are coupled, which means that upon changing one stream the total mass balance for all streams has to be recalculated and fed again into the programme. Further input parameters are the concentrations of the components in the ore, the distribution coefficients of these components for the HH and DH and the wash efficiency, discussed in section 3.4.

The output of the computer model consists of the mass flows and concentrations of all components in the different process streams. In this paper only the concentrations in the product acid (PA), the hemihydrate (HH), the recrystallization liquor (CL) and the dihydrate (DH) are discussed. The conversion liquor (CL) composition is representative for the concentrations in the dihydrate section.

3. RESULTS AND DISCUSSION

3.1. Verification of the model

The concentrations of the macro and micro components in the four above mentioned streams of the HDH process of Hydro Agri Rotterdam B.V. (HAR) were simulated with the computer model and compared with analyzed concentrations in the real process.

As input for the computer model the actual total mass flows are used. Because the total mass flows of the streams 9, 11 and 21 were only approximately known, these flows were optimized in the program to render the best fitting values for the mass balances of P and Zn in the HAR process. For a best fit a wash efficiency of 0.55 was found.

Subsequently the mass balances were calculated for the components Ca, S, Cd, Fe, Al, La and U, using their concentrations in the ore and their distribution coefficients in HH and DH as input parameters. In this way simulated concentrations of all components in the HH, DH, PA and CL were compared with the concentrations obtained by analysis of the actual process streams. The best fit between the two data sets was achieved by adaptation of the concentration in the ore and the distribution coefficients. Only small adaptations in those input parameters were needed, so in spite of all the assumptions the model serves as a satisfactory tool to predict the different concentrations in the outgoing process streams.

Typical differences of 5 % between calculated and actual concentrations in the PA, HH, DH and of maximally 50 % in the CL streams (see table 2) can be ascribed to: I) errors in the sampling and analysis of the samples II) errors in the process streams III) and the fact that the assumptions in the model are not completely obeyed by the actual process.

The larger differences between the concentrations of some of the components in the rock used as input parameters of the model and their simulated values are caused by apparently too large errors in the sampling and analysis of the samples, given the discrepancy between the measured masses of these minor components entering and leaving the process. When for example from the ore analysis the input of lanthanum through the ore is calculated (3.3 kg La/hr), this amount appears to be considerably smaller than the output through the dihydrate and phosphoric acid (9.4 kg La/hr) even when the output through the wash water which is attached to the dihydrate, is neglected. To reduce the differences better analyses of some trace components are therefore desired.

3.2. The HH process compared to the HDH process

In this section the concentrations in the outgoing streams of a HH process are compared with those of a HDH process.

In table 3 the compositions of the HH and the product acid, PA, are given for both processes, for the same ore, the same flows and the same distribution coefficients.

Because of the recrystallization of the HH in the HDH process more phosphate (P) per amount kg ore is available per kg product acid, due to i) the lower incorporation of phosphate in DH than in HH and ii) the higher water content of the DH compared to HH which leaves less water diluting the phosphoric acid.

In practice the wash water of a HH process (indicated in table 3 with an asterix) is adapted to obtain phosphoric acid with 18.3 % P. In table 3 the concentrations of the components in the HH* and PA* are shown for the case where the amount of wash water is correspondingly reduced from 53 to 44 ton/hr.

Table 2 The concentrations of different components in the ore, the hemihydrate (HH), product acid (PA), dihydrate (DH) and recrystallization liquor (CL) as analyzed (A) and simulated with the computer model (M) for a HDH process.

	P (%)		Ca (%)		S (%)		Zn (ppm)		Cd (ppm)	
	A	M	A	M	A	M	A	M	A	M
ore	14.9	14.9	35.8	35.9		"	92	106	4.9	6.5
HH	0.74	0.75	27.6	27.7	22.2	22.2	2.6	2.5	2.2	3.0
PA	18.5	18.6	0.21	0.21	0.23	0.23	135	133	5.7	6.1
DH	0.039	0.042	23.2	23.2	18.6	18.7	0.2	0.21	1.0	0.9
CL	2.9	3.0	0.33	0.33	0.073	0.074	15.6	16.2	4.9	4.4
	Fe(%)		Al(%)		La(ppm)		U(ppm)			
	A	M	A	M	A	M	A	M		
ore	0.13	0.19	0.11	0.08	55	160	75	40		
HH	0.006	0.008	0.19	0.25	123	124	68	67		
PA	0.23	0.24	0.053	0.050	0.041	0.041	6.8	6.7		
DH	0.003	0.003	<0.05	<0.05	103	104	13	18		
CL	0.07	0.03	0.74	0.48	1.8	1.9	74	89		

¹⁾ The ingoing sulfuric acid stream (Φ_2) is used to calculate the sulfuric acid concentrations.

Table 3. The concentrations in the product acid (PA) and the hemihydrate (HH) and the P loss via the disposed calcium sulfate slurry as simulated with the computer model for a HH and HDH process. HH* is a HH process with 20 % less wash water.

	HH process		HH* process		HDH process	
	PA	HH	PA*	HH*	PA	DH
P %	16.6	0.67	18.4	0.79	18.6	0.042
Zn ppm	127	2.4	141	2.7	133	0.21
Cd ppm	4.4	2.1	4.6	2.3	6.1	0.9
Fe %	0.22	0.007	0.24	0.013	0.24	0.0023
Al %	0.011	0.053	0.011	0.053	<0.05	<0.05
La ppm	0.04	123	0.04	123	0.041	104
U ppm	2.9	29	2.9	29	6.7	18
P loss %	5.8		6.7		2.3	

A consequence of the higher P content in the product acid resulting from the lower wash water flow, is a higher phosphate loss via the HH, i.e. 6.7 % vs. 5.8 %. The most efficient process however is the HDH process with only 2.3 % phosphate loss. Also with respect to the minor components a cleaner calcium sulfate byproduct is achieved in the HDH process, although it has to be kept in mind that the reduction in disposal depends on the distribution coefficients of both HH and DH, as will be shown in section 3.7.

3.3. Influence of filter efficiency

In a HDH process scheme the total mass flows 9, 11 and 21 are determined by the filter efficiency of the first and third filter sections of the HH filter and of the third filter section of the DH filter respectively. The filter efficiency is defined as the mass fraction of dry crystals in the wet filter cake and is determined by the filterability of the crystals and by the filter itself. Because the filterability of calcium sulfate crystals can vary widely, by a factor of 10, the influence of variations in these streams on the concentrations of the process flows has to be known.

In Fig. 5 to Fig. 8 the concentrations of phosphorus and cadmium are given in the PA, CL, HH and DH process streams as a function of the filter efficiency of the first section of the HH filter. These figures demonstrate that a variation in the filter efficiency has a large impact on the phosphate concentrations and on the phosphate loss and that therefore the filterability of the HH crystals should be kept well under control. Due to the relatively high incorporation of cadmium in the hemihydrate, compared to phosphate, the small amount of liquor in the wet filter cake can hardly influence the total amount of cadmium in the wet filter cake, resulting in only a small influence of the filter efficiency on the cadmium concentrations.

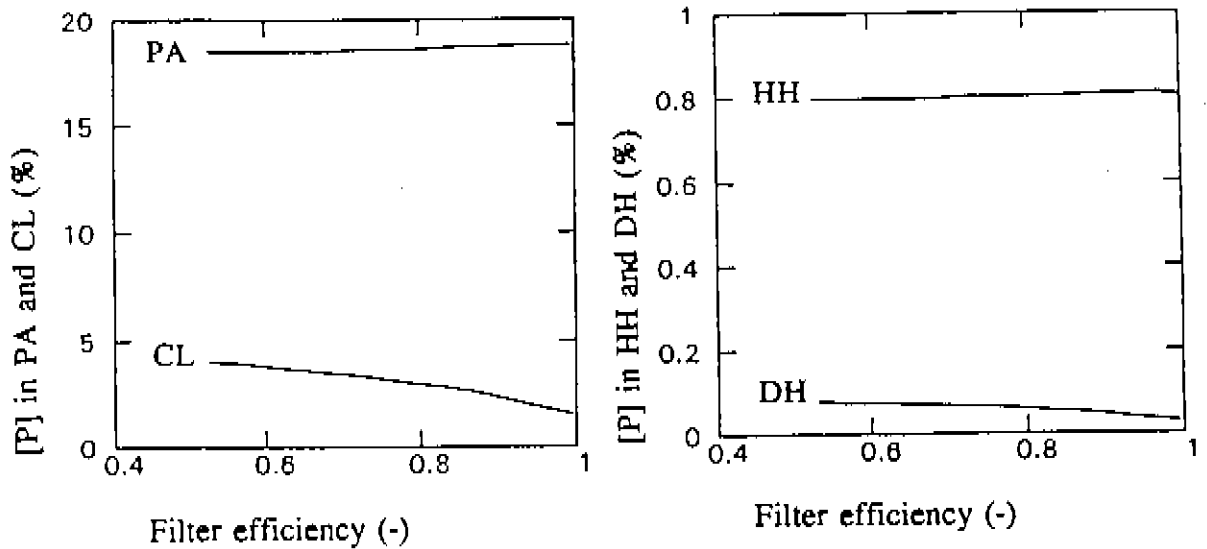


Fig. 3 and 4 The influence of the filter efficiency of the first HH filter section on the phosphate concentrations in PA, CL, HH and DH.

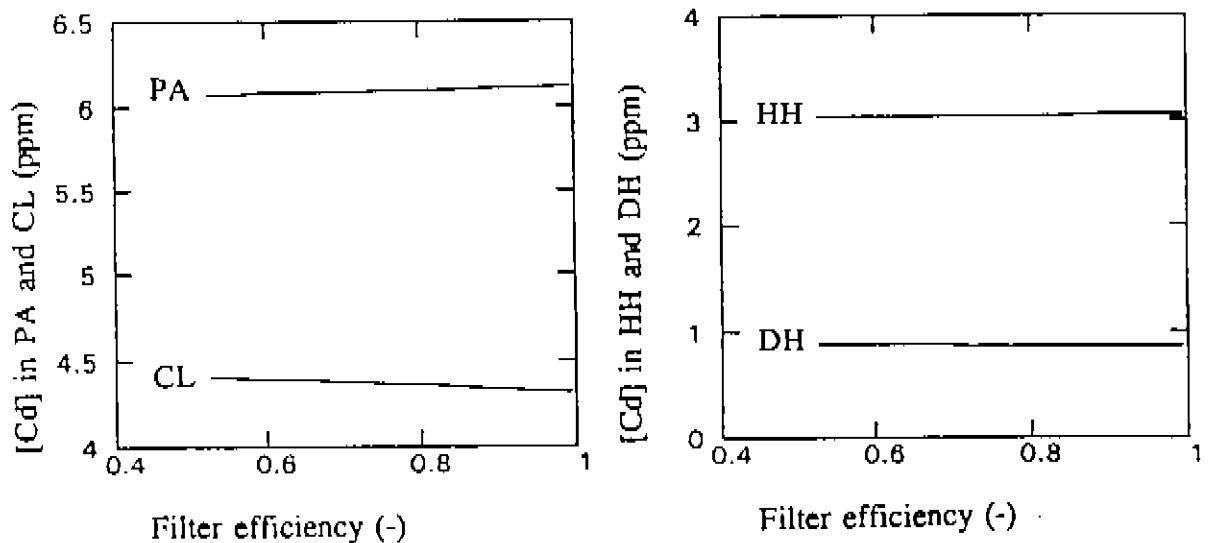


Fig. 5 and 6 The influence of the filter efficiency of the first HH filter section on the cadmium concentration in PA, CL, HH and DH.

The filter efficiencies of the third section of the HH filter and of the DH filter only have a minor influence on the concentrations in the PA, CL, HH and DH process streams. For typical filter efficiencies between 0.6 and 0.8 the phosphate concentrations in the CL increase maximally 10%.

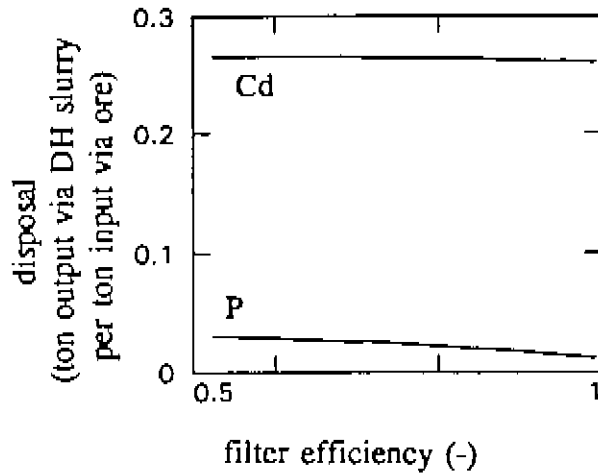


Figure 7 The phosphorus and cadmium disposal as a function of the filter efficiency of the first filter section of the HH filter.

3.4. Wash efficiency

In the case of a wash efficiency of 0.5 the concentrations of the micro components in the wash water (ϕ_{ww} in Fig. 8), leaving the filter section, equal their concentrations in the liquor attached to the dry filter cake (ϕ_{fc} in Fig. 8).

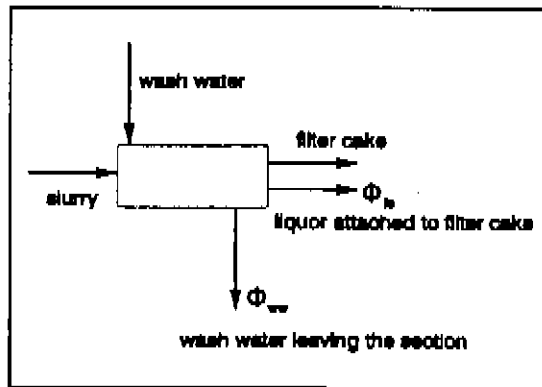


Figure 8 A filter section.

However, in case of shortcircuiting the concentrations in ϕ_{fc} will be higher than the concentrations in ϕ_{ww} , whereas the concentrations in ϕ_{fc} are much lower than the concentrations in ϕ_{ww} when the attached liquor passes the filter cake like a plug flow. The wash efficiency WE is defined as

$$WE = \frac{\phi_{ww}}{\phi_{fc} + \phi_{ww}} \quad (4)$$

WE=0 describes shortcircuiting and WE=1 describes plug flow washing. In Fig. 9 to Fig. 14 the influence of the wash efficiency on the concentrations in the outgoing flows and CL is shown by changing WE from 0.1 to 1.

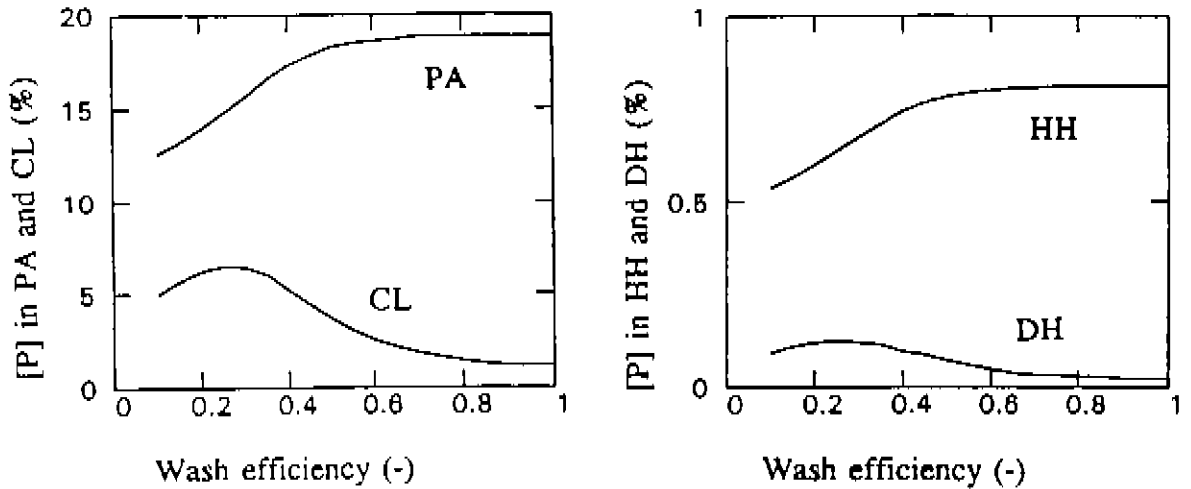


Fig. 9 and 10 Phosphate concentration in PA, CL, HH and DH as a function of the wash efficiency.

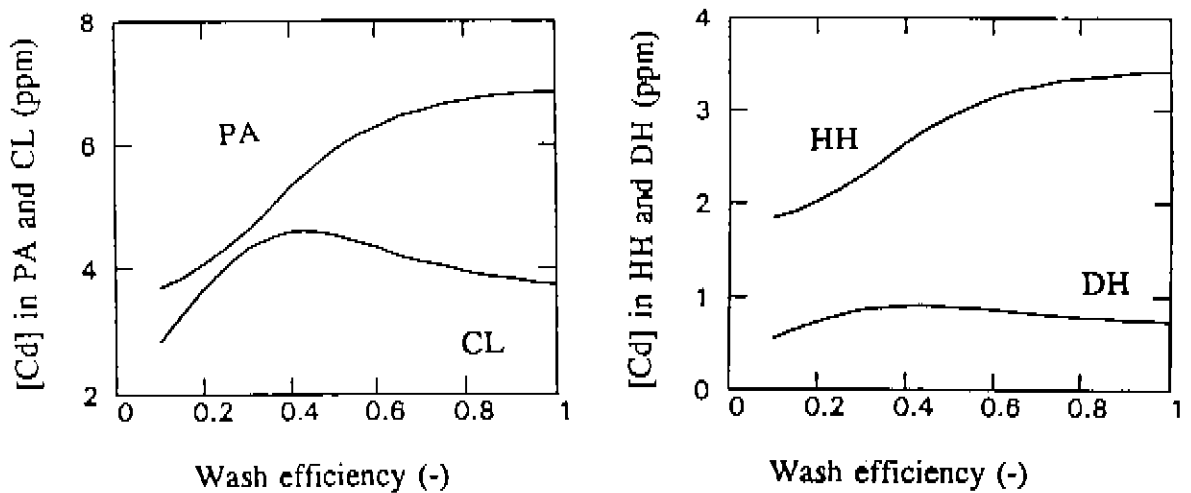


Fig. 11 and 12 Cadmium concentration in PA, CL, HH and DH as a function of wash efficiency.

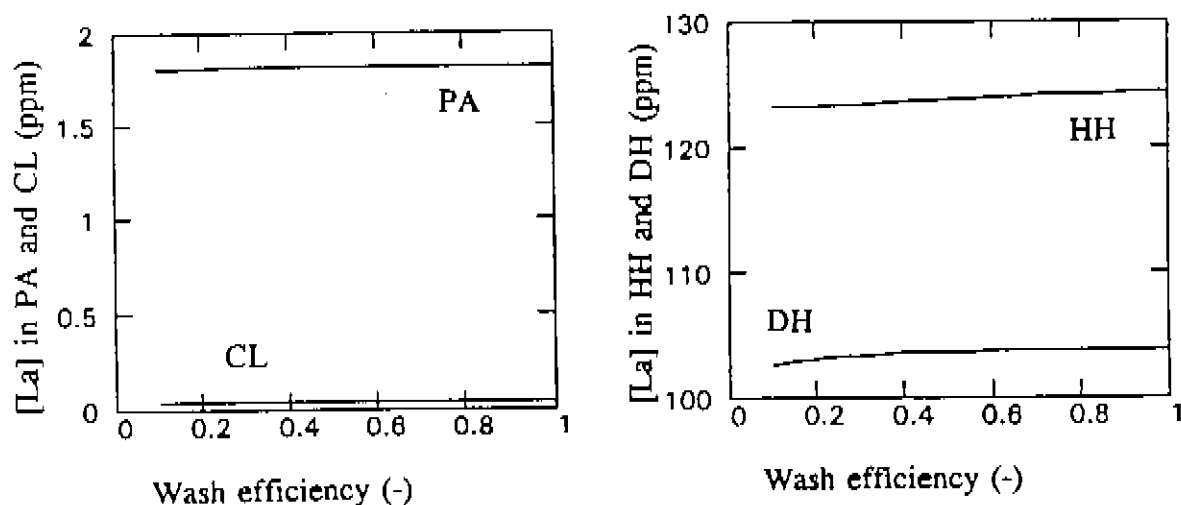


Fig. 13 and 14 Lanthanum concentration in PA, CL, HH and DH as a function of wash efficiency.

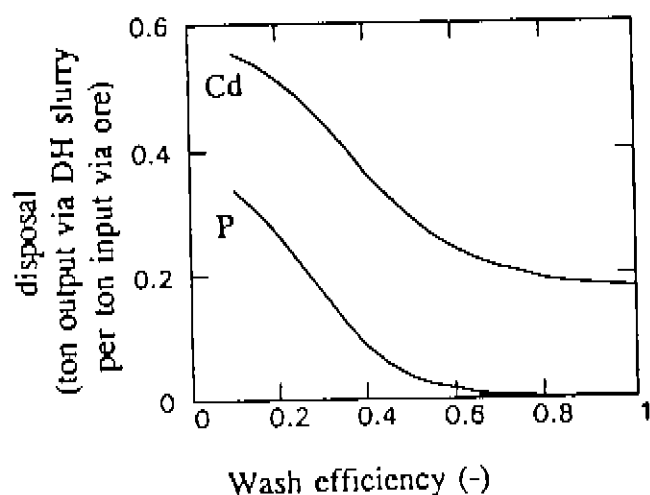


Figure 15 Fraction P and Cd of the ore in the disposed DH slurry as a function of wash efficiency.

These figures show the large impact of the wash efficiency on the concentrations of phosphate and cadmium in the different streams, whereas the influence on the lanthanum concentration is negligible. Figure 15 shows that a large decrease in phosphate and cadmium disposal can be achieved by a high value for WE.

3.5. Incomplete or unwanted conversions

3.5.1. Incomplete digestion

The digestion of the ore is between 99 and 100 percent under normal process conditions. A digestion below 98 percent makes the phosphoric acid process economically unacceptable.

Incomplete digestion has two major effects. First the undigested ore incorporates in the hemihydrate and is not dissolved under the conditions prevailing in the recrystallization reactor. It thus remains as unreacted ore with the dihydrate instead of forming phosphoric acid. Therefore, the uptake of phosphate by the DH increases and the H_3PO_4 content of the phosphoric acid decreases.

Secondly, the mass flow of the stream from the hemihydrate reactor to the filter and of the product acid and calcium sulfate decreases slightly (up to 2 % in case of 98 % digestion), while the sulfuric acid concentration in the entering stream ϕ would easily double (4 % in case of 98 % digestion) if no precautions are taken. In practice the sulfuric acid dosage is accordingly reduced to avoid high sulfuric acid concentrations which easily leads to blinding of the ore by encapsulation of the digestion ore particles with a HH layer. This worsens incomplete digestion.

To account for incomplete digestion in the model the total mass flows are adjusted in such a way that the amount of solids and phosphoric acid remain unchanged.

Incomplete digestion has a major influence on the phosphate concentrations in the solids (for DH an increase of 400 % in case of 98 % digestion), which is caused by the low distribution coefficients in HH as well as in DH causing the concentration in the undigested ore to be high compared to the concentrations in the DH.

The influence of the degree of digestion on the concentrations of micro components in DH will be most prominent for components with low distribution coefficients.

3.5.2. Incomplete recrystallization from hemihydrate to dihydrate

In the presence of certain impurities, such as lanthanides [4] or aluminum fluoride [5,6], the recrystallization can be seriously retarded, causing an incomplete conversion of HH into DH. Here the effect of conversions between 50 and 100 percent upon the P, Cd and La concentrations in the streams PA, HH, CL and DH and on the fraction P, Cd and La in the disposed DH slurry will be discussed.

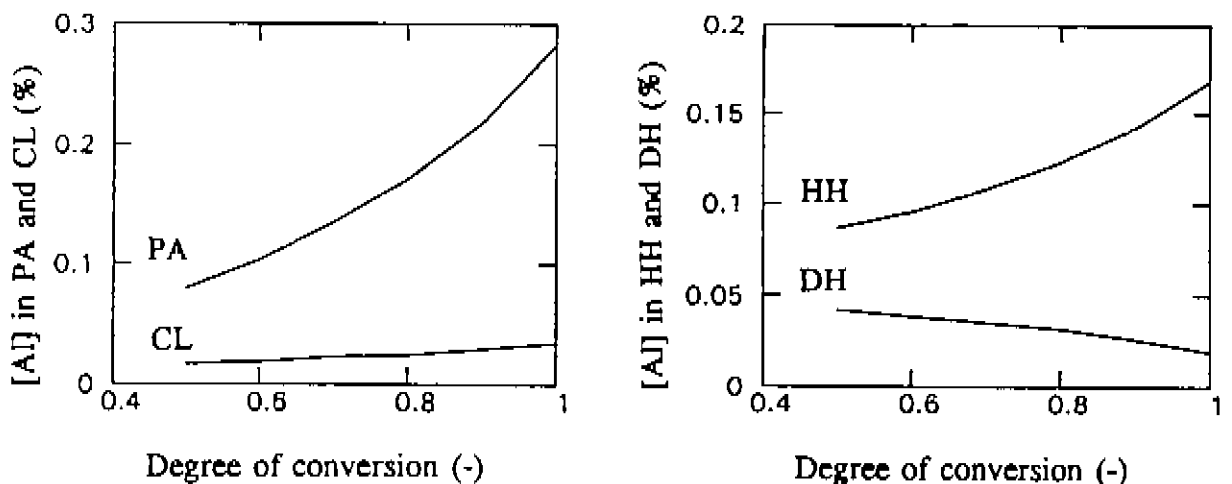


Fig. 16 and 17 The aluminium concentration in PA, CL, HH and DH as a function of the degree of conversion.

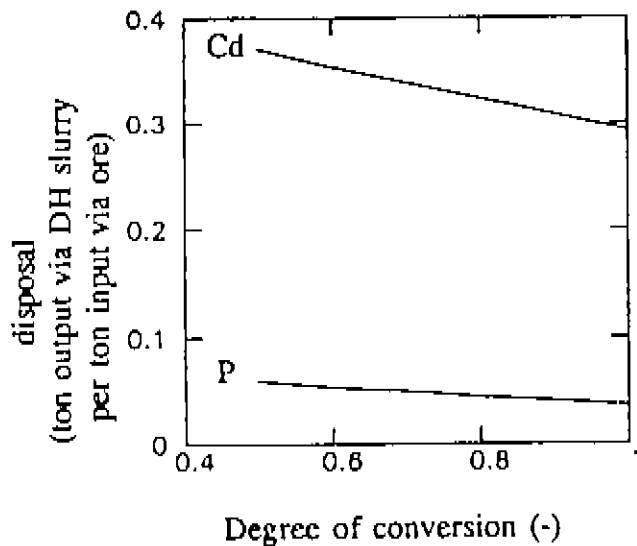


Figure 18 The influence of the degree of conversion on the disposal of cadmium and phosphate.

From calculations it follows that for most components the influence of the degree of conversion on the concentrations in all discussed process streams is negligible, except for the dihydrate. Only if the distribution coefficient in HH is much higher than in DH the concentrations in other streams are changed dramatically as can be seen in Figure 16 and 17, where the influence on the aluminium concentrations in PA, CL, HH and DH is demonstrated.

Incomplete recrystallization on the concentrations in DH results in an enhanced disposal through the DH slurry, as can be seen from Figure 18.

3.5.3. Formation of anhydrite in the hemihydrate reactors

If locally high temperatures (above 100 C) are reached or if locally high sulfuric acid concentrations (above 4 %) are formed due to poor mixing conditions anhydrite can develop. In general anhydrite formation is unfavourable because the uptake of some micro components and especially of cadmium is much higher in anhydrite than in dihydrate or hemihydrate. Incidental misoperations in the plant may lead to the formation of up to 5 percent anhydrite in the hemihydrate reactor.

Once anhydrite is formed, it can not be transformed in the recrystallization tank, since it is the most stable calcium sulfate phase under the given process conditions.

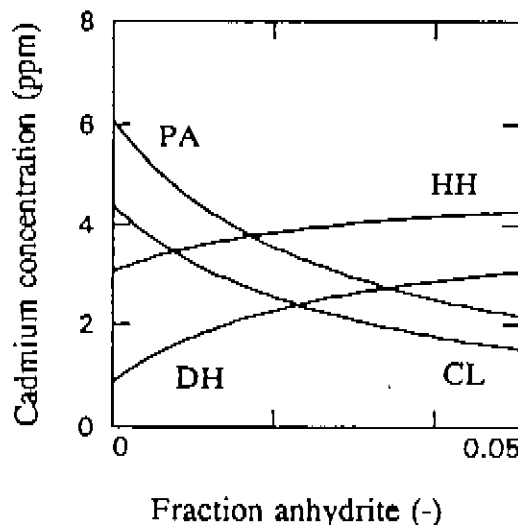


Figure 19 The concentrations in the HH, DH, PA and CL (in ppm) as a function of the fraction formed anhydrite.

In Figure 19 the simulated concentrations of cadmium in the hemihydrate, dihydrate, product acid and conversion liquor are plotted as a function of the anhydrite formation in a system with 6.5 ppm cadmium in the ore and distribution coefficients of 0.5, 0.2 and 30 for hemihydrate, dihydrate and anhydrite respectively [7]. From this figure it can be seen that the presence of anhydrite increases the incorporation of cadmium in both solid phases considerably, especially the uptake in the dihydrate. Formation of anhydrite therefore has to be avoided, if strict regulations for the purity of the gypsum are imposed. The formation of anhydrite can on the other hand be used if only the quality of phosphoric acid is of importance, because 5 percent anhydrite formation can already reduce the cadmium concentration in the phosphoric acid by more than 50 percent for the given distribution coefficients.

3.6. Sensitivity of impurity uptake in DH for variations in K_{HH} and K_{DH} values

Until now, only a given HDH configuration with fixed distribution coefficients has been discussed. The distribution coefficients of many components can, however, be changed by the presence of impurities like aluminium fluoride or lanthanides, via their influence on the nucleation and growth kinetics of the HH or DH crystals. For this reason the introduction of another type of ore, with for instance a different aluminum, silicon or lanthanides content, could induce a change in the distribution coefficient of a number of micro components. Here the influence of variations in the distribution coefficients K for HH and DH on the final outlet of micro components via the dihydrate and the product acid will be demonstrated. This influence is best reflected by an disposal number, defined as the impurity output (in kg/hr) via the dihydrate (DN) divided by the input (kg/hr) through the ore. In fig. 20 the disposal number is shown as a function of K_{HH} and K_{DH} for the HDH process. For the HH process the disposal number is defined in a similar way for the impurity outlet via the HH. If the wash liquor attached to the solids which also contains a certain amount of impurities are taken into account even higher DN values are obtained, as indicated in Figure 21.

In Figure 20 and 21 also the disposal number of a HH process with exactly the same mass flows is given. Comparison of the HH with the HDH process shows that the disposal number of the HDH process is higher if the distribution coefficient in DH is lower than approximately three times the distribution coefficient in HH. In most cases the K_{DH} is even lower than the K_{HH} , so in general the disposal number of the HDH process is lower than of a HH process.

Figure 21 shows that in all cases the disposal number on wet filter cake basis and, therefore, the actual disposal is lower for the HDH process compared to the HH process.

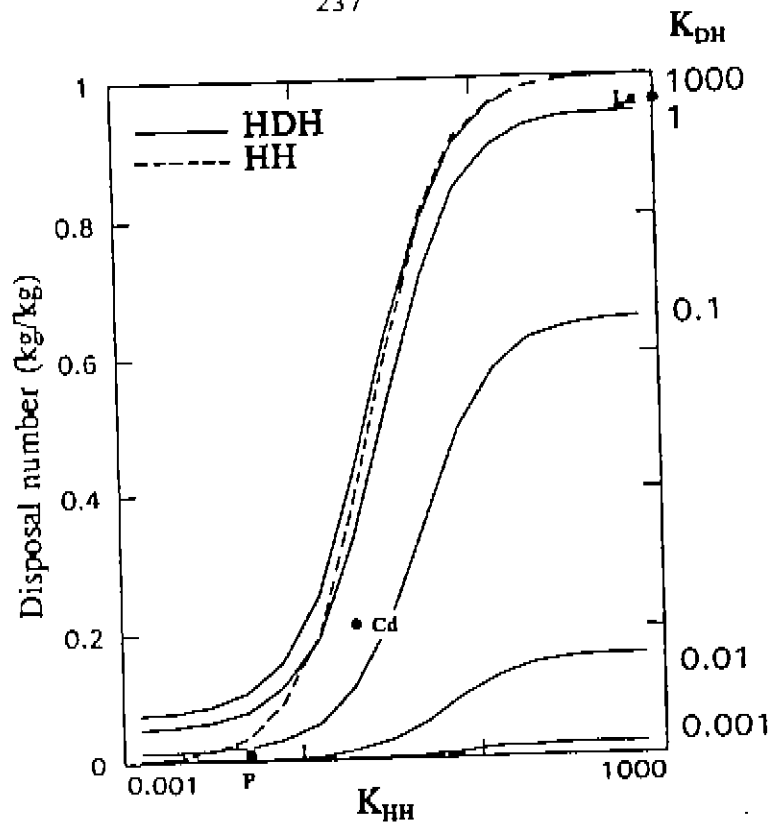


Figure 20 Disposal number on basis of dry cake as a function of K_{HH} and K_{DH} for both processes. The K_{HH} and K_{DH} for P, Cd and La are shown too.

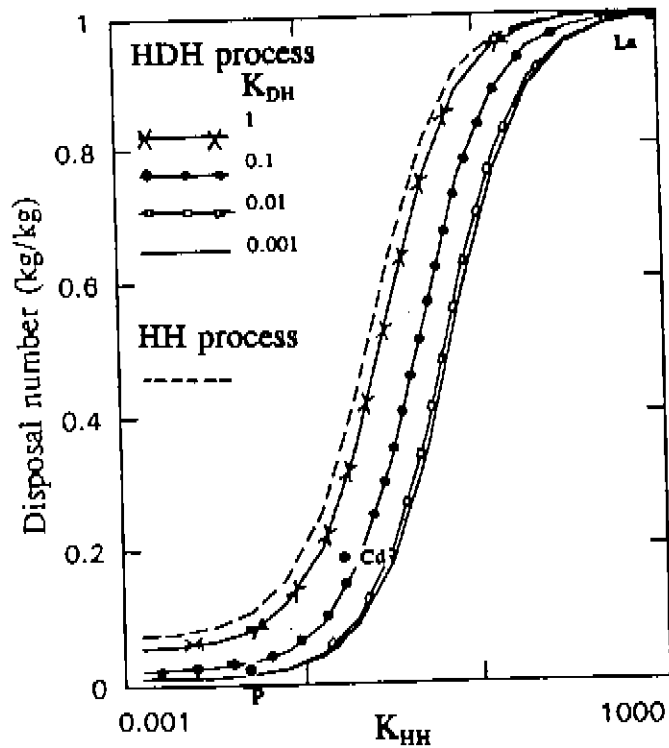


Figure 21 Disposal number (on slurry basis) as a function of K_{HH} and K_{DH} for both processes. The K_{HH} and K_{DH} for P, Cd and La are shown too.

4. CONCLUSIONS

The HH and HDH process can be described well on the basis of a simplified flow scheme with mass balances, using distribution coefficients to represent the uptake of impurities by the HH and DH crystals. These simple mass balances are very useful to investigate the effect of changes in the process on the distribution of impurities entering the process with the ore over the various outlet streams. Changes which can be imposed on the process are for example adaptations in wash water flows or dosage of additives which influence the distribution coefficients of other impurities.

This mass balance program can further be used as a tool to optimize the different process flows or to predict and optimize the disposal of micro components through the product acid or the calcium sulfate.

Computer simulations confirm that a HDH process produces a cleaner calcium sulfate dihydrate which has a higher phosphate efficiency compared to HH process. A good filterability of the HH crystals and a high wash efficiency leads to lower impurity and phosphate levels in the outgoing streams.

Incomplete digestion has a large impact on components like phosphates, which are not incorporated very well in the calcium sulfate.

Incomplete recrystallization mainly increases the concentrations of the impurities in the dihydrate.

Anhydrite formation has a large impact on the concentrations of micro components like cadmium, with a relatively high distribution coefficient in anhydrite compared to the distribution coefficients in hemihydrate and dihydrate.

A sensitivity analysis as described in par. 3.6 allows determination of the effect of a change in distribution coefficients in either the hemihydrate or the dihydrate on the disposal through the dihydrate or hemihydrate. The sensitivity analysis shows that the disposal

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Appendix 1. The mass balances of the HDH process (according figure 1)

The model calculates the mass flows i (Φ_i) of a component, using the total mass flows ($\Phi_{i,tot}$), the distribution coefficient for HH and DH (K_{HH} and K_{DH}) and the slurry recycle ratio from tank B to A (recycleration).

The mass balances over the digestion/HH crystallization section are described by equation 5 to 8.

$$\Phi_3 = \Phi_1 + \Phi_4 + \Phi_5 \quad (5)$$

$$\Phi_5 = \text{recycleration} * \Phi_6 \quad (6)$$

$$\Phi_6 = \Phi_3 - \Phi_5 \quad (7)$$

$$\Phi_{HH} = K_{HH} * \Phi_{HH,tot} * \frac{\Phi_7}{(\Phi_{9,tot} + \Phi_{10,tot})} \quad (8)$$

Equation 9 to 18 show the mass balances over the HH filter

$$\Phi_{12} = \Phi_{HH} + \frac{\Phi_7}{(\Phi_{9,tot} + \Phi_{10,tot})} * (\Phi_{6,tot} - \Phi_{9,tot} - \Phi_{10,tot} - \Phi_{HH,tot}) \quad (9)$$

$$\Phi_7 = \Phi_6 - \Phi_{12} \quad (10)$$

$$\Phi_9 = \Phi_7 - \Phi_{10} \quad (11)$$

$$\Phi_{10} = \frac{\Phi_{10,tot}}{\Phi_{9,tot}} * \Phi_9 \quad (12)$$

$$\Phi_8 = \Phi_{11} + \Phi_{12} - \Phi_{13} \quad (13)$$

$$\Phi_{13} = \Phi_{HH} + \frac{\Phi_8}{\Phi_{8,tot}} * (\Phi_{6,tot} - \Phi_{9,tot} - \Phi_{10,tot} - \Phi_{8,tot} + \Phi_{11,tot} - \Phi_{HH,tot}) \quad (14)$$

$$\Phi_4 = \Phi_8 + \Phi_9 \quad (15)$$

$$\Phi_{11} = \Phi_{13} + \Phi_{14} - \Phi_{15} \quad (16)$$

$$\Phi_{15} = \Phi_{HH} + \frac{\Phi_{11}}{\Phi_{11,tot}} * (\Phi_{6,tot} - \Phi_{9,tot} - \Phi_{10,tot} - \Phi_{8,tot} + \Phi_{14,tot} - \Phi_{HH,tot}) \quad (17)$$

$$\Phi_{17} = \Phi_{15} + \Phi_{16} \quad (18)$$

Equation 19 describes the mass balance over the recrystallization section, while the mass balance over the DH filter is described by equation 20 to 25.

$$\phi_{DH} = K_{DH} * \phi_{DH,tot} * \frac{\phi_{14}}{\phi_{14,tot}} \quad (19)$$

$$\phi_{20} = \phi_{DH} + \frac{\phi_{14}}{\phi_{14,tot}} * (\phi_{19,tot} - \phi_{14,tot} - \phi_{DH,tot}) \quad (20)$$

$$\phi_{14} = \phi_{17} + \phi_{20} \quad (21)$$

$$\phi_{22} = \phi_{DH} + \frac{\phi_{16}}{\phi_{16,tot}} * (\phi_{19,tot} - \phi_{14,tot} - \phi_{16,tot} + \phi_{21,tot} - \phi_{DH,tot}) \quad (22)$$

$$\phi_{16} = \phi_{21} + \phi_{20} - \phi_{22} \quad (23)$$

$$\phi_{21} = \phi_{22} + \phi_{23} - \phi_{24} \quad (24)$$

$$\phi_{24} = \phi_{DH} + \frac{\phi_{21}}{\phi_{21,tot}} * (\phi_{19,tot} - \phi_{14,tot} - \phi_{16,tot} + \phi_{23,tot} - \phi_{DH,tot}) \quad (25)$$

The influences of the filter, wash, digestion or recrystallization efficiencies as well as the influence of the anhydrite formation on the concentrations in the process streams are calculated with altered mass balances. As an example the changed mass balance equations are given for the case that the influence of the wash efficiency on the concentrations in the process streams is investigated.

$$\phi_{13} = \phi_{HH} + \frac{\phi_8}{\phi_{8,tot}} * (\phi_{6,tot} - \phi_{9,tot} - \phi_{10,tot} - \phi_{8,tot} + \phi_{11,tot} - \phi_{HH,tot}) * \frac{1-WE}{WE} \quad (26)$$

$$\phi_{15} = \phi_{HH} + \frac{\phi_{11}}{\phi_{11,tot}} * (\phi_{6,tot} - \phi_{9,tot} - \phi_{10,tot} - \phi_{8,tot} + \phi_{14,tot} - \phi_{HH,tot}) * \frac{1-WE}{WE} \quad (27)$$

$$\phi_{22} = \phi_{DH} + \frac{\phi_{16}}{\phi_{16,tot}} * (\phi_{19,tot} - \phi_{14,tot} - \phi_{16,tot} + \phi_{21,tot} - \phi_{DH,tot}) * \frac{1-WE}{WE} \quad (28)$$

$$\phi_{24} = \phi_{DH} + \frac{\phi_{21}}{\phi_{21,tot}} * (\phi_{19,tot} - \phi_{14,tot} - \phi_{16,tot} + \phi_{23,tot} - \phi_{DH,tot}) * \frac{1-WE}{WE} \quad (29)$$