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USE OF CHLORIDE-CONTAINING HYDROMETALLURGICAL WASTEWATERS FOR PRODUCTION OF DILUTE HYDROCHLORIC ACID

The original method has been proposed for the dilute HCl production by two-step regeneration of the exhausted ion-exchange resin in the chloride form, resulting from the treatment of chloride-containing hydrometallurgical wastewaters. The method includes application of the aqueous solution of H_2SO_4 in regeneration of the exhausted anion-exchange resin in the first step and washing of the regenerated resin with pure water in the second step. It results in the reduction of the sulfuric acid consumption and in significant out-down of the HCl production cost as compared with the traditional methods using H_2 and Cl_2. Experimental results using Hungarian pyridine-based anion-exchange resin VARION AP have been presented and discussed in details.

Dilute hydrochloric acid is very often used for regeneration of ion-exchange resin in hydrometallurgical plants. As a result of the processes following the regeneration, different waste products containing chlorides are obtained which usually are not reused.

In this paper the use of chloride-containing wastewaters obtained in hydrometallurgical plants for production of dilute hydrochloric acid is considered. For this purpose ion-exchange resin in chloride-form — obtained either during the sorption or by treatmnent with chloride-containing wastewater — is required.

Production of dilute hydrochloric acid from the above-mentioned materials proceeds according to the following chemical reactions:

$$R-Cl + H_2SO_4 \rightleftarrows R-HSO_4 + HCl, \tag{1}$$

$$2R-HSO_4 \overset{\text{water}}{\rightleftarrows} R_2SO_4 + H_2SO_4, \tag{2}$$

$$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-}. \tag{3}$$

Process (1) takes place when the dilute sulfuric acid is applied for the regeneration of the exhausted resin in the chloride form, whereas process (2) proceeds when the regenerated ion-exchange bed is fed with pure water.

From the formulae (1) and (2) it can be seen that for the production of one mole of hydrochloric acid only 0.5 mole of sulfuric acid is required taking into consideration the sulfuric acid "regained" in reaction (2). However, in practice more sulfuric acid is neces-

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sary, because according to the authors studies the value of equilibrium constant of the process (2) is of order of 10^{-2}. This is the main advantage of the method proposed by authors as compared to the production of hydrochloric acid according to reaction (1) in which one mole of sulfuric acid is needed for one mole of hydrochloric acid [1].

In the investigations the domestic (Hungarian) pyridine-based ion-exchange resin VARION AP was used. The solution containing suitable concentration of ions examined has been shaken together with ion-exchange resin for 24 hours (in proportion 100 : 1 = solution : resin). After separation of the resin from the solution applying of vacuum filtration, the resin has been analysed for chlorides, sulfates, and hydrogen sulfates by suitable methods.

2. STUDY OF THE CHLORIDE—HYDROGENSULFATE EXCHANGE EQUILIBRIUM

Equilibrium data concerning the ion-exchange process described by equation (1) are given in tab. 1. From the data presented it is obvious that hydrogensulfate ions are sorbed more strongly by the ion-exchange resin VARION AP than the chloride ions; the value of the selectivity constant is:

$$\beta = \frac{D_{HSO_4^-}}{D_{Cl^-}} \approx 1.4,$$

thus in countercurrent system the chloride content in the resin can be regained in form of hydrochloric acid by applying sulfuric acid, at the same time, however, the sulfate content in the hydrochloric solution can be held at a very low value in case of suitable number of stages.

Table 1

Data on chloride-hydrogensulfate exchange equilibrium

Dane dotyczące równowagi wymiany jonowej: chlorek-kwaśny siarczan

Sample number	Solution phase g-eq/dm³		Resin phase g-eq./dm³	
	Cl^-	HSO_4^-	Cl^-	HSO_4^-
1	0.1	0.9	0.079	1.259
2	0.3	0.7	0.231	1.069
3	0.5	0.5	0.4051	0.9345
4	0.7	0.3	0.6254	0.7053
5	0.9	0.1	0.8352	0.4904

3. RECOVERY OF SULFURIC ACID FROM THE RESIN IN HYDROGENSULFATE FORM

Resin in hydrogensulfate form in presence of water will be partly converted into sulfate form according to the reaction (2). Equilibrium of the process can be characterized by the data presented in fig. 1. As ion-exchange resin contains about 120—130 g of hydrogensulfate ions/dm³, the concentration of the sulfuric acid in the solution may be about 18—23 g/dm³, i.e. a part of sulfuric acid sorbed by the resin in form of hydrogensulfate may be recovered in countercurrent system.

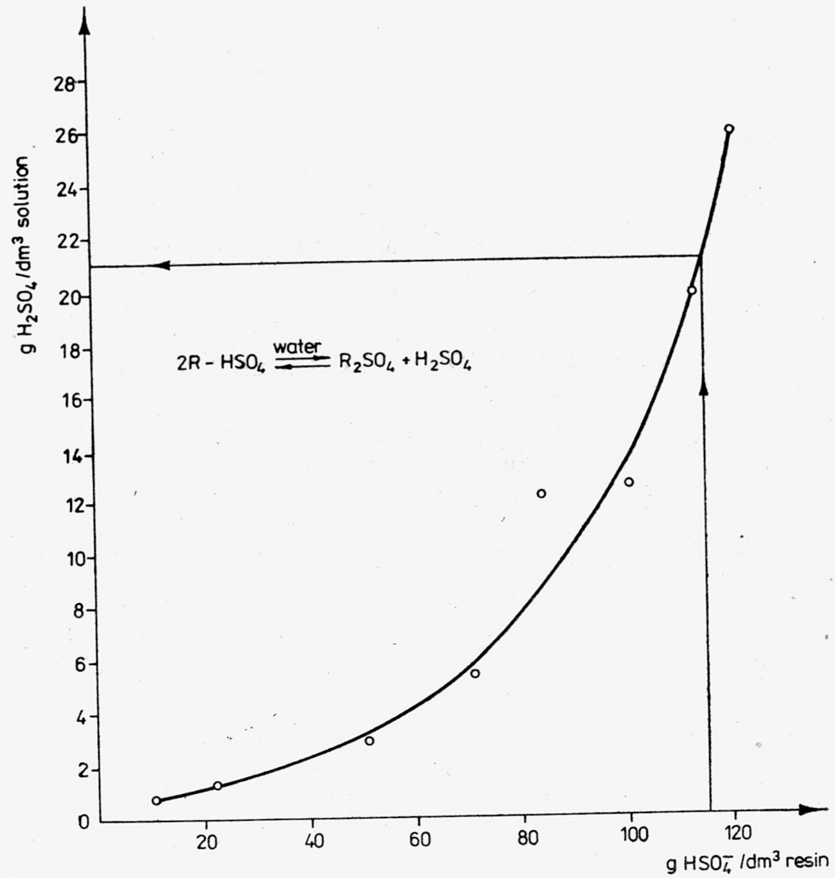

Fig. 1. Distribution of the sulphuric acid between anion-exchange resin and aqueous phase

Rys. 1. Rozdzielenie kwasu siarkowego między anionitem i fazą wodną

4. STUDY OF THE SULFATE–CHLORIDE EXCHANGE EQUILIBRIUM

Sorption of the chloride from the wastewater solutions by ion-exchange resin can be characterized by the chemical reaction (3). The data regarding the equilibrium of the reaction are given in tab. 2. They show that under the circumstances examined chloride is very well sorbed by the ion-exchange resin, thus the resin in sulfate form may be easily converted in countercurrent system into resin in chloride form, from which hydrochloric acid can be produced according to the process (1).

Table 2

Data on the sulfate–chloride exchange equilibrium

Dane dotyczące równowagi wymiany siarczan–chlorek

Sample number	Solution phase g-eq./dm^3		Resin phase g-eq./dm^3	
	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}
1	0.1	0.9	0.369	0.879
2	0.3	0.7	0.853	0.483
3	0.5	0.5	1.080	0.224
4	0.7	0.3	1.201	0.101
5	0.9	0.1	1.286	0.023

5. CONTINUOUS COUNTERCURRENT TESTS

Full process of hydrochloric acid production based on the above-mentioned equilibrium has been examined in a pilot scale.

5.1. PRODUCTION OF HYDROCHLORIC ACID FROM SULFURIC ACID BY RESIN IN CHLORIDE FORM

Test results of the reactions (1) and (2) occurring in countercurrent system are schematically presented in fig. 2. Data concerning material flows, retention period, and concentration are also given in this figure. They prove that dilute hydrochloric acid solution with very low sulfate content can be produced on the basis of the above-mentioned method.

5.2. PRODUCING OF RESIN IN CHLORIDE FORM FROM CHLORIDE-CONTAINING WASTE SOLUTIONS

Resin in sulfate form can be most suitably converted into chloride form with chloride-containing solution using countercurrent column technique. If, however, the solution contains the ions forming precipitate with the sulfate ions, e.g. calcium ions, then

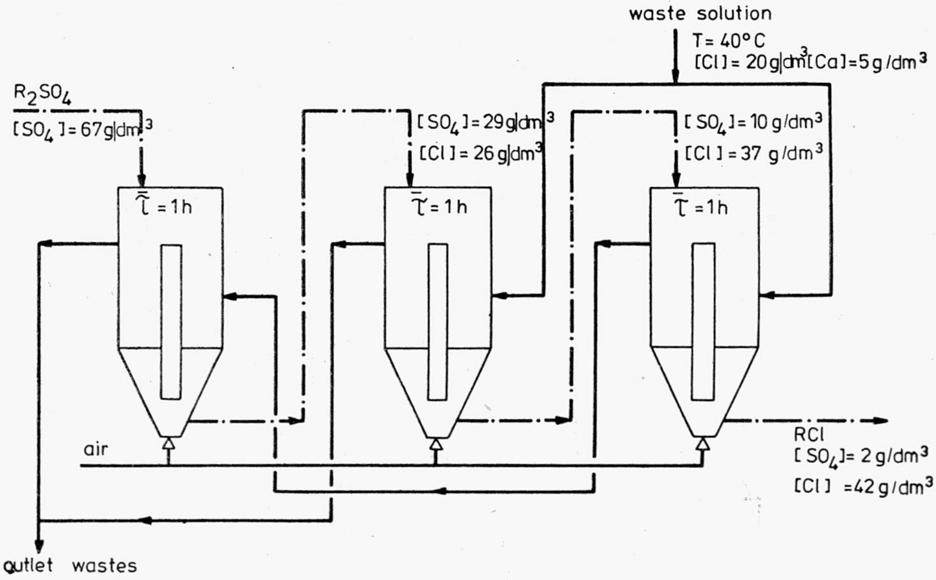

Fig. 3. Production of resin in chloride form in tank reactors (resin: liquid phase ratio = 1 :2.5)

Rys. 3. Produkcja jonowymieniacza w formie chlorku w reaktorach (stosunek żywicy do formy płynnej = 1 :2,5)

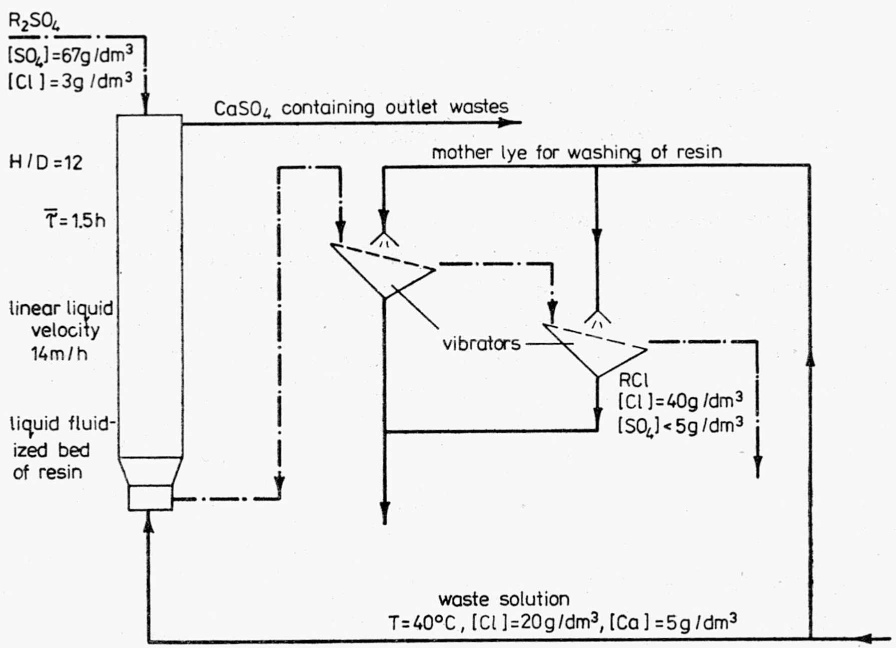

Fig. 4. Production of resin in chloride form liquid fluidized bed (resin: liquid phase ratio = 1 :4.5)

Rys. 4. Produkcja jonowymieniacza w formie chlorku w płynnym złożu fluidalnym (stosunek żywicy do formy płynnej = 1 :4,5)

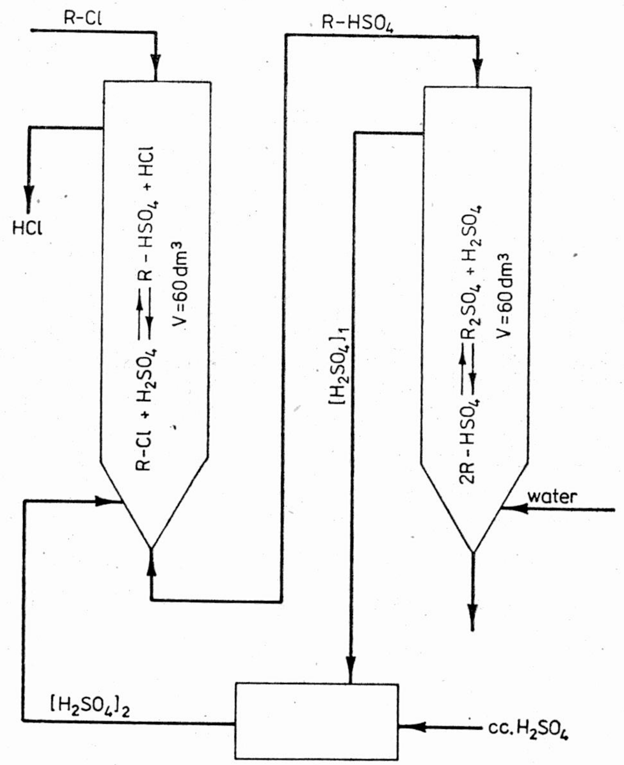

Fig. 2. Principal scheme of obtaining of dilute hydrochloric acid

Rys. 2. Zasadniczy schemat otrzymywania rozcieńczonego kwasu solnego

moving packed bed technique cannot be applied, because of the bed clogging with the precipitating gypsum. In such case the process described by reaction (3) must be performed in a fluidized bed column or special tank reactors. Results achieved by applying the reactors and fluidized bed columns are given in figs. 3 and 4, respectively.

From these data it may be concluded that resin in the chloride form with low sulfate content can be gained from chloride-containing wastewater solutions.

6. SUMMARY

Based on the above experimental results an industrial scale system has been constructed for production of hydrochloric acid. The cost of hydrochloric acid produced in this way is significantly lower than that of acid produced by the traditional method using H_2 and Cl_2.

REFERENCES

[1] OSBORN G., *Synthetic ion exchangers*, Mir, Moscow 1964, p. 199.

WYKORZYSTANIE ŚCIEKÓW HYDROMETALURGICZNYCH ZAWIERAJĄCYCH CHLOR DO PRODUKCJI ROZCIEŃCZONEGO KWASU SOLNEGO

Zaproponowano oryginalną metodę produkcji kwasu solnego za pomocą dwustopniowej regeneracji wyczerpanego jonitu, który otrzymano w postaci chlorku powstałego w wyniku oczyszczania ścieków hydrometalurgicznych zawierających chlorki. W pierwszym stopniu tej metody stosuje się wodny roztwór kwasu siarkowego do regeneracji wyczerpanego anionitu, a w drugim — zasila się zregenerowany jonit czystą wodą. Zmniejsza to w efekcie zużycie kwasu siarkowego oraz obniża w znacznym stopniu koszty produkcji HCl w porównaniu z metodami tradycyjnymi, w których stosuje się wodór i chlor. Przedstawiono i szczegółowo omówiono wyniki doświadczeń, w których stosowano węgierski anionit VARION AP bazujący na pirydynie.

NUTZUNG DER HYDROMETALLURGISCHEN, CHLORHALTIGEN ABWÄSSER ZUR HERSTELLUNG VON VERDÜNNTER SALZSÄURE

Vorgeschlagen wird eine HCl-Herstellungsmethode durch zweistufige Regeneration von chlorhaltigen Ionenaustauschern, die im Reinigungsprozeß von hydrometallurgischen Abwässern entstehen. In der ersten Stufe wird dem erschöpften Anionit eine wässrige H_2SO_4-Lösung zugesetzt, in der zweiten Stufe wird der regenerierte Ionenaustauscher mit reinem Wasser gespeist. Das vermindert den H_2SO_4-Verbrauch und die Produktionskosten der Salzäure im Vergleich zu der traditionellen Methode, wenn H_2 und Cl_2 verwendet werden.

Eingehend werden Versuchsergebnisse besprochen, in denen ein ungarischer Anionit VARION AP, auf Pyridin gestützt, zur Anwendung kam.

ИСПОЛЬЗОВАНИЕ ГИДРОМЕТАЛЛУРГИЧЕСКИХ СТОЧНЫХ ВОД, СОДЕРЖАЩИХ ХЛОР ДЛЯ ПРОИЗВОДСТВА РАЗБАВЛЕННОЙ СОЛЬНОЙ КИСЛОТЫ

Предложен своеобразный метод производства HCl с помощью двухстадийной регенерации отработанного ионита, который был получен в виде хлорида, образовавшегося в результате очистки гидрометаллургических сточных вод, содержащих хлориды. На первой стадии этого метода применяется водный раствор H_2SO_4 для регенерации отработанного анионита, а на второй стадии регенированный ионит питается чистой водой. Это уменьшает в эффекте потребление H_2SO_4, а также в значительной степени снижает стоимость производства HCl по сравнению с традиционными методами, в которых применяется H_2 и Cl_2. Представлены и подробно обсуждены результаты испытаний, в которых применялся венгерский анионит VARION AP, базирующийся на пиридине.