BALANCE MODEL OF THE NEUTRALIZATION OF ACID WASTE WATER FROM CHEMICAL POLISHING OF GLASS

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The acid waste water, containing for the most part sulphuric, hydrofluoric and hexafluorosilicic acids, is neutralized with an aqueous supension of technical-grade calcium hydroxide (milk of lime). The balance model allows the capacity of interoperation tanks and that of the neutralization reactors to be calculated. The waste water is produced by rinsing chemically polished glass ware with water. The effect of the number of interoperation rinses on the production of acid waste water and on the capacity of interoperation tanks is demonstrated. The model is suitable for small waste water neutralizing stations whose design in this country has till recently been a purely empirical matter. Correct operation of such plants is an indispensable prerequisite for environmental protection of the neighbourhood of glass polishing shops where acid waste water is produced.

INTRODUCTION

Neutralization of acid waste water from chemical polishing of glass is the basic chemical operation in the process of disposal of the respective harmful substances arising in the operation. Technical-grade calcium hydroxide in the form of the milk of lime is curently used as the neutralizing agent. The neutralizing reactions yield the so-called neutralization sludge. The actual neutralization of the acid waste water, containing dissociated mineral acids as its main components (H_2SO_4, HF and H_2SiF_6), can be described by the following schematic equations:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\,H_2O \qquad (1)$$

$$2\,HF + Ca(OH)_2 \rightarrow CaF_2 + 2\,H_2O \qquad (2)$$

$$H_2SiF_6 + 4\,Ca(OH)_2 \rightarrow CaSiO_3 + 3\,CaF_2 + 5\,H_2O. \qquad (3)$$

The acid waste water arises by passage of the polishing bath, containing the acids mentioned above, into the water used in rinsing the polished glass. Chemical polishing of lead glass results in the dissolution of a surface layer of the ware, approximately 100 μm in thickness, yielding water-soluble, poorly soluble and virtually insoluble salts. The insoluble salts constitute the so-called primary sludge.

THEORY

In designing the neutralizing station, one has first to determine the capacity of interoperation tanks, reactors and the sludge separating equipment (filterpress, centrifuge). The way of separating the sludge depends, among others, on the possibility of utilizing it as a secondary raw material. The choice of a suitable neutralization reactor, either for continuous or discontinuous operation, is also significant. The kinetics of neutralization of dilute sulphuric acid with the milk of lime is affected, among other factors, also by the compostion of the technical-grade hydrated lime, in particular by its content of carbonate. A study of the course of neutralization of acid waste water in an industrial mixed reactor with a capacity of 6 m^3 showed that a batch can be neutralized within about 2 hours. The mean time of residence during neutralization of acid waste water in a continuous industrial mixed rector of 10 m^3 capacity was established at 1.5 hour. Attainment of stoichiometric consumption of the hydrated lime also depends on the way the equivalence point is indicated. At many small neutralizing stations, the pH has so far been measured with pH indicating papers instead of using precise instrumentation, with the result that the waste water has mostly a distinctly alkaline reaction.

A schematic diagram of a neutralizing station is shown in Fig. 1. It is assumed that the acid waste water is produce continuously. The Z_1 interoperation

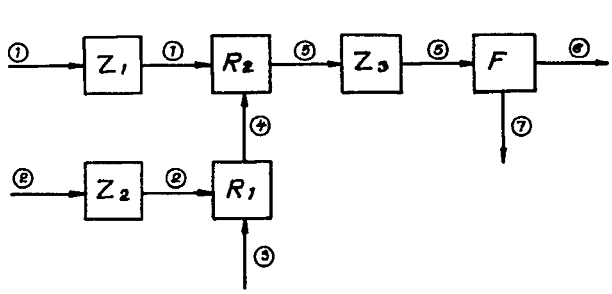

Fig. 1. Schematic diagram of a neutralizing station.
1 – acid water, 2 – lime, 3 – fresh water, 4 – milk of lime, 5 – neutralization sludge, 6 – waste water, 7 – filter cake, Z_1 – acid water tank, Z_2 – powder lime bin, Z_3 – neutralization sludge tank, R_1 – tank for preparation of milk of lime, R_2 – neutralization reactor, F – filterpress.

Table I

Dependent (Y) and independent (X) values of the balance model

Variable	Unit	Description
X_1	1	weight fraction of solid phase in milk of lime
Y_2	kg m^{-3}	density of milk of lime
Y_3	kg m^{-3}	density of acid water
X_4	1	weight fraction of H_2SO_4 in acid water
Y_5	m^3	volume of tank Z_1 for acid water
X_7	d^{-1}	number of shifts
Y_8	m^3 d^{-1}	volume flow of milk of lime
X_9	1	weight fraction of HF in acid water
X_{10}	1	weight fraction of H_2SiF_6 in acid water
X_{11}	d	time of operation from lime stock in Z_2
Y_{12}	kg	capacity of lime tank Z_2
Y_{13}	kg d^{-1}	material flow through reactor R_2
Y_{14}	kg d^{-1}	material flow of dry neutralization sludge
Y_{15}	kg d^{-1}	material flow of moist neutralization sludge (filter cake)
Y_{16}	1	weight fraction of free water in filter cake
Y_{17}	kg d^{-1}	material flow of waste water
Y_{18}	kg h^{-1}	output of filter press in material flow of filter cake
X_{19}	h	time of filtration per shift
Y_{20}	m^3	volume of continuous reactor R_2
X_{21}	h	mean residence time in continuous reactor R_2
Y_{22}	m^3	volume of batch reactor R_2
Y_{23}	m^3	volume of batch reactor R_1
Y_{24}	kg h^{-1}	output of filterpress – filtrate
X_{25}	kg	weight of glass polished in one operation
X_{26}	1	weight fraction of K_2O in glass
X_{27}	1	weight fraction of Na_2O in glass
X_{28}	1	weight fraction of glass transferred to polishing bath
X_{29}	1	weight fraction of PbO in glass
Y_{30}	kg d^{-1}	material flow of polishing sludge from glass polished (mainly $PbSO_4$)
X_{31}	1	number of rinses of glass during polishing process
X_{32}	kg	weight of acid water from one rinse
Y_{33}	kg d^{-1}	material flow of acid water to neutralization process
X_{34}	min	polishing time
X_{35}	min	rinsing time
Y_{36}	d^{-1}	number of polishing operations
Y_{37}	kg d^{-1}	material flow of glass polished
Y_{38}	1	weight fraction of CaF_2 in dry neutralization sludge
Y_{39}	1	weight fraction of $CaSiO_3$ in dry neutralization sludge
Y_{40}	m^3	volume of tank Z_3
X_{41}	h	mean residence time in tank Z_3

tank serves as a surge tank for acid water to be neutralized. The capacity of tank Z_2 determines the stock of the milk of lime for the neutralizing station. Reactor R_1 for the preparation of milk of lime is usually of the discontinuous type. Its capacity can be determined according to the consumption of lime per shift, etc. The neutralizing reactor, R_2, may be continuous or discontinuous; its capacity depends on the type. Interoperation tank Z_3 for neutralization sludge suspension equalizes the throughputs of neutralization reactor R_2 and filter F, possibly has to meet additional technological requirements, and serves as a sludge settling tank.

Balance model of the neutralizing station

The model is based on a weight balance of the system supplemented with stoichiometry of the neutralizing reactions and dissolution of glass. Table I lists the variables of the balance model. There are two types of the variables : independent ones (model input values) and dependent ones (model output values). Quantity X_7 given in Table I specifies the utilization rate of the neutralizing station on the assumption of 8 hours per shift. Input quantity X_{11} determines the capacity of the hydrated lime storage bin for the given time of requested pre-stocking. Input quantity X_{19} specifies the net time of filtering the sludge suspension per shift. Quantity X_{28} expresses the amount of glass passed dissolved in the polishing bath and eventually passed into the acid water by the polishing process. Quantity X_{34} gives the time of polishing including the time of handling the glass products.

The balance model comprises the following equations:

$$Y_2 = (100X_1 + 154.37)/0.15558 \quad (4)$$

$$Y_3 = 734.79X_4 + 994.3 \quad (5)$$

$$Y_5 = Y_{33}(32 - 8X_7)/24Y_3 \quad (6)$$

$$Y_8 = Y_{33}(X_4M_1/M_2 + X_9M_1/2M_3 + X_{10}4M_1/M_7) \quad (7)$$

$$Y_{12} = X_{11}Y_8 \quad (8)$$

$$Y_{13} = Y_{33} + Y_8Y_2 \quad (9)$$

$$Y_{14} = Y_{33}(X_4M_6/M_2) + X_9M_5/M_2 + X_{10}(3M_5 + M_4)/M_7 \quad (10)$$

$$Y_{15} = Y_{14}/(1 - X_{16}) \quad (11)$$

$$Y_{17} = Y_{33}(1 - (X_4 + X_9 + X_{10})) + Y_8Y_2(1 - X_1) - Y_{15}X_{16} \quad (12)$$

$$Y_{18} = Y_{15}/(X_{19}X_7) \quad (13)$$

$$Y_{20} = (Y_{33}/Y_3 + Y_8)X_{21}/8X_7 \quad (14)$$

$$Y_{22} = (Y_{33}/Y_3 + Y_8)/X_7 \quad (15)$$

$$Y_{23} = Y_8/X_7 \quad (16)$$

$$Y_{24} = Y_{13}/(X_7X_{19}) - Y_{18} \quad (17)$$

$$Y_{30} = Y_{37}X_{28}(X_{26}M_8/M_{10} + X_{27}M_9/M_{11} + X_{29}M_{12}/M_{13}) \quad (18)$$

$$Y_{33} = Y_{36}X_{31}X_{32} \quad (19)$$

$$Y_{36} = 8X_7/((X_{31}X_{35} + X_{34})/60) \quad (20)$$

$$Y_{37} = Y_{36}X_{25} \quad (21)$$

$$Y_{38} = Y_{33}(X_9M_5/2M_3 + X_{10}3M_5/M_7)/Y_{14} \quad (22)$$

$$Y_{39} = Y_{33}(X_{10}M_4/M_7)/Y_{14} \quad (23)$$

$$Y_{40} = (Y_{33}/Y_3 + Y_8)X_{41}/8X_7 \quad (24)$$

According to equation (6), the capacity of interoperation acid water tank Z_1 is calculated so that at single-shift operation of neutralization the Z_1 tank be capable of accommodating the entire one-day production of acid water; at three-shift operation, the accumulating capacity of tank Z_1 should be equivalent to one-shift production of acid water. The capacity of discontinuous reactor Y_{22} is calculated for processing the aliquot proportion of daily acid water production in a single charge. Because the time of neutralizing one charge (2 hours) is shorter than the length of one shift, a reserve in the capacity of the neutralization reactor is available.

The capacity of the continuous reactor is considered for a mean residence time X_{21} = 3 hrs., which again represents an output reserve of the reactor. The capacity of interoperation tank Z_3, calculated from equation (24), is given by the requirement for the mean time of residence of the sludge suspension, X_{41}. Using equations (23) and (19), the capacity of filter F is calculated on the assumption that all of the liquid phase passed through the neutralization reactor

Table II

Input values of the blance model – accuracy ± 5%, relative

Variable	Value	Unit
X_1	0.15	1
X_4	0.08	1
X_7	2	1
X_9	0.001	1
X_{10}	0.001	1
X_{11}	14	d
X_{16}	0.23	1
X_{19}	4	h
X_{21}	3	h
X_{25}	100	kg
X_{26}	0.123	1
X_{27}	0.019	1
X_{28}	0.05	1
X_{29}	0.24	1
X_{31}	1	1
X_{32}	300	kg
X_{34}	50	min
X_{35}	5	min
X_{41}	5	h

Table III Output values of the balance model

Variable	Value	Unit	Accuracy ± %, rel.
Y_2	1087	kg m^{-3}	0.4
Y_3	1053	kg m^{-3}	0.3
Y_5	2.8	m^3	7.3
Y_8	1.7	m	11.4
Y_{12}	3986	kg	11.2
Y_{13}	6329	kg d^{-1}	9.1
Y_{14}	641.5	kg d^{-1}	10.1
Y_{15}	833.1	kg d^{-}	10.2
Y_{17}	5489	kg d^{-1}	9.1
Y_{18}	104.1	kg h^{-1}	10.2
Y_{20}	1.1	m^3	9.1
Y_{22}	2.9	m^3	7.6
Y_{23}	0.87	m^3	10.3
Y_{24}	687	kg h^{-1}	9.1
Y_{30}	49.6	kg d^{-1}	9.7
Y_{33}	4431	kg d^{-1}	8.9
Y_{36}	14.8	1	5.7
Y_{37}	1480	kg d^{-1}	7.6
Y_{38}	0.025	1	5.9
Y_{39}	0.005	1	6.9
Y_{40}	1.86	m^3	9.1

Table IV

Capacity and output parameters of the basic components of the neutralizing station

Symbol of component	Capacity	Output
Z_1	2.8 m^3	
Z_2	3986 kg	
Z_3	1.86 m^3	
R_1	0.87 m^3	
R_2 continuous	1.17 m^3	
R_2 batch	2.98 m^3	
F		104.1 kg h^{-1} of filter cake
F		687 kg h^{-1} of filtrate

a) production of acid water 4431 kg d^{-1}

Table V

Influence of X_{31} on the parameters of the neutralizing station

	X_{31}		
Parameter	1	2	2.5
Y_{33} kg d^{-1}	4431	8229	9931
Y_{15} kg d^{-1}	833	1547	1867
Y_{37} kg d^{-1}	1480	1370	1324
Y_{30} kg d^{-1}	50	46	44
Z_1 m^3	2.8	5.2	6.3
Z_2 kg	3986	7400	8934
Z_3 m^3	1.9	3.5	4.2
R_1 m^3	0.87	1.62	1.96
R_2 m^3 batch	3	5.5	6.7
R_2 m^3 cont.	1.2	2.1	2.5
F kg h^{-1} filter cake	104	193	233
F kg h^{-1} filtrate	687	1276	1540

is filtered. The balance model was resolved by means of the KOMAT program [3,4] which is capable of determining the accuracy of dependent variables on the basis of the accuracy of input values.

PRACTICAL EXAMPLE

Table II lists the values of input variables for the balance calculation. The values indicate that the initial concentration of solid phase in the milk of lime amounts to 15 wt.%, the acid waste water contains 8 wt.% H_2SO_4, 0.1 wt.% HF and 0.1 wt.% H_2SiF_6. The glass being polished contains 24 wt.% PbO, 12.3 wt.% K_2O and 1.9 wt.% Na_2O. The rinsing operation yields 300 kg of acid water. The shift rate $X_7 = 2$, that is 16 hours of operation of the neutralizing station daily.

Table III gives the results of balance calculation using the input quantities from Table II. Table III shows that the daily production amounts to 4431 kg of acid water and 641.5 kg of dry neutralization sludge or 833.1 kg of this sludge containing 23 wt.% of free water. The total daily production of waste water from neutralization is 5489 kg and that of dry matter of primary sludge is 49.6 kg.

Table IV lists the capacity and throughput parameters of the individual items of equipment of the neutralizing station. The number of rinses of the polished glass affects decisively the production of waste polishing water. One rinse represents the technology of polishing glass without intermediate rinsing, that is using a single rinse after the chemical polishing. Two rinses correspond to one intermediate rinse and one rinse after polishing, etc. Table V illustrates the effect of the number of rinses (parameter X_{31})

on the technological parameters, capacity dimensions and throughput of the neutralization facilities on the assumption of a constant composition of the acid water. Generally, parameter X_{31} may acquire arbitrary values, but practically only positive integers. Table V demonstrates that with increasing X_{31}, the production of acid water increases, that of acid water (Y_{37}) decreases and the capacity demands on storage tanks and reactors grow.

CONCLUSION

The present study was concerned with a neutralizing station model based on a weight balance of the system. In view of the fact that neutralization of acid waste water from polishing is a part of a complete system designed for reducing or eliminating the toxicity of waste materials produced by chemical polishing of glass, a balanced and proportional design of all items of the station is a necessary prerequisite for maintaining ecological safety of the operation. As the technical and technological standard of a number of neutralizing stations is quite poor, in particular in the case of small works, their ecological safety is likewise unsatisfactory. The present paper should therefore draw attention to the necessity of subjecting the small and so far underestimated neutralizing stations to careful chemico-engineering analyses. Following adjustments according to the specific local conditions, the ballance model described may be applied to any arbitrary process involving neutralization of acid waste water containing acids which form insoluble sludge with calcium hydroxide.

List of symbols

d	–	day
F	–	filterpress
M_1	–	molecular weight
i	=	1 – $Ca(OH)_2$, 2 – H_2SO_4, 3 – HF, 4 – $CaSiO_3$, 5 – CaF_2, 6 – $CaSO_4.2H_2O$, 7 – H_2SiF_6, 8 – K_2SiF_6, 9 – Na_2SiF_6, 10 – K_2O, 11 – Na_2O, 12 – $PbSO_4$, 13 – PbO
R	–	reactor
Z	–	tank

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BILANČNÍ MODEL NEUTRALIZACE KYSELÉ VODY Z CHEMICKÉHO LEŠTĚNÍ SKLA

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Kyselá voda obsahující kyselinu sírovou, fluorovodíkovou a hexafluorokřemičitou je neutralizována suspenzí technického hydroxidu vápenatého ve vodě. Modelem lze stanovit kapacitu mezioperačních zásobníků a kapacitu neutralizačního reaktoru. Zdrojem kyselé vody je oplachování leštěných skleněných výrobků vodou. Je ukázán vliv počtu mezioplachů na produkci kyselé vody a na kapacitu mezioperačních zásobníků. Model je vhodný pro malé neutralizační stanice kyselých vod, jejichž projektování bylo v našich podmínkách ještě zcela nedávno založeno na empirii; přitom správná funkce malé neutralizační stanice je důležitou podmínkou ochrany životního prostředí v okolí malých průmyslových zdrojů kyselých vod.

Obr. 1. Schéma neutralizační stanice.
1–kyselá voda, 2–vápenný hydrát, 3–voda užitková, 4–vápenné mléko, 5–neutralizační suspenze, 6–odpadní voda, 7–neutralizační kal, Z_1–zásobník kyselé vody, Z_2–zásobník práškového vápenného hydrátu, Z_3–zásobník suspenze z neutralizace, R_1–reaktor na výrobu vápenného mléka, R_2–neutralizační reaktor, F–filtrační zařízení.