

Mercury removal from contaminated mud coming from chlor-alkali plant

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ABSTRACT

The paper considers the problem of decontamination of mud coming from a chlor-alkali plant. The mud heavily polluted by mercury has been analysed in order to ascertain the solid phases and the modalities of mercury association. Taking into consideration the characteristics of mercury in respect to the inert association of solid components of the mud, a laboratory-scale thermal-based process has been developed. The volatile products coming from thermal treatment have been captured in suitable traps in order to avoid any diffusion of the metal into the atmosphere, thus ensuring safe environmental conditions. Material balance ascertained before and after the treatment process indicates success of the operation which provides a silt and sand product containing mercury at a level lower than that fixed for acceptance of the material for reuse in land restoration. © 2004 SDU. All rights reserved.

Keywords: Mercury; Mud pollution; Thermal treatment

1. INTRODUCTION

Chlor-alkali plants, using mercury cathodes, are still used today to produce chlorine by electrolysis. These plants generate a mud heavily polluted by mercury (Habashi, 1999). Hence the advantage offered by the high concentration of caustic soda produced by the plant is offset by the disadvantage of the environmental impact resulting from mercury-induced pollution (Pasquon and Guerrieri, 1985). Due to its high vapour pressure mercury readily diffuses in the atmosphere and under organic speciation affects the life-chain up to the level of the human being (Habashi, 1999).

The toxic effects of this metal and its compounds on living organisms relate particularly to the nervous system, kidney and liver (Habashi, 1999; Japan Public Health Association, 2001).

2. EXPERIMENTAL

The mud under study comes from a former chlor-alkali plant operating in Italy. It has the aspect of a compact clay mass with a water content of about 24%. After drying at low temperature (50°C), to avoid evaporation of the mercury, the sample was gently disaggregated in order to obtain a size distribution of less than 850µm. Size-analysis carried out on the sample shows that most of the material (85% by weight) is finer than 5µm. This fraction was analysed by a laser particle-size analyser. The resulting size distribution is plotted in Figure 1.

The mineral association in the mud was determined by X-ray analysis carried out by means of a Siemens diffractometer. The mineralogical phases were found were calcite, gypsum, quartz and clay minerals such as montmorillonite, muscovite and kaolinite.

Thermal analysis (TGA-DTA), shown in Figure 2, confirms the presence of calcite, as evidenced by the endothermic effect at temperatures above 600°C when there is a loss in weight due to decomposition of the calcite. The loss of weight between 200°C and 500°C, and relative exothermic effect, reveal the presence of organic material.

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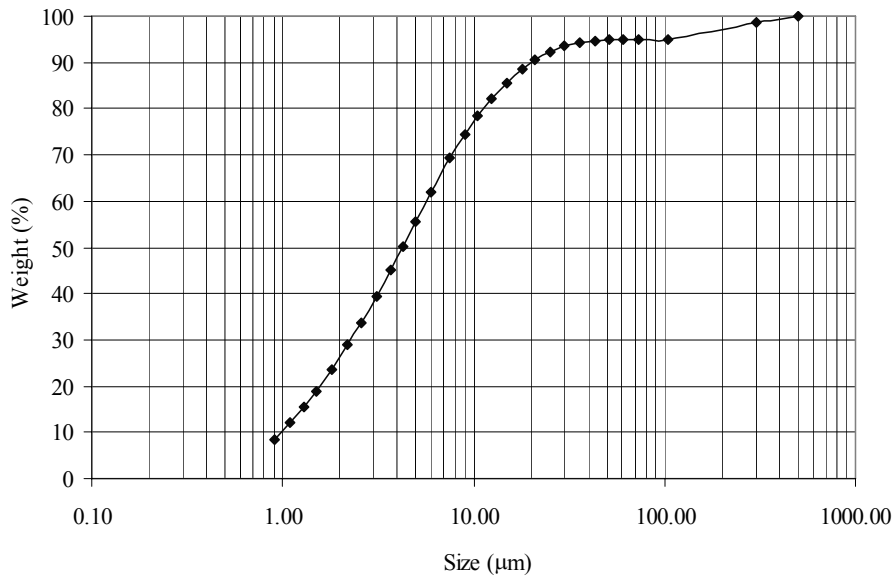


Figure 1. Size distribution of the mud sample

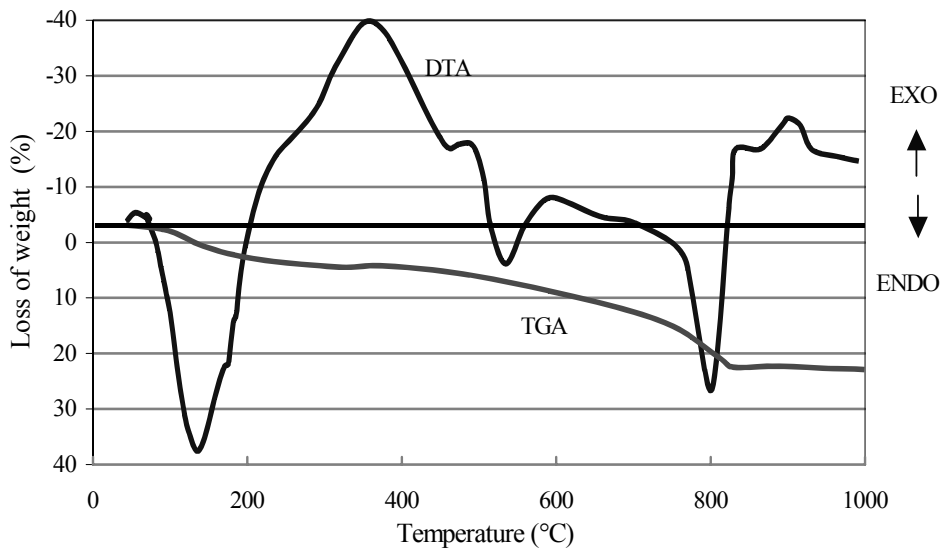


Figure 2. Thermogram of the <850µm size fraction of the polluted sediment (TGA= thermo-gravimetric plot; DTA= thermo-differential plot)

Hg distribution in the size-fractions was determined by an AMA 254 (Advanced Mercury Analyser from Altec Ltd). As shown in Table 1, most of the Hg is concentrated in the finest fraction but all fractions appear to have a mercury content exceeding the limits allowed by the Italian regulations (5ppm for soils involved in commercial and industrial installations and 1ppm for soils re-used in public green-spaces).

Table 1
 Size analysis of mud and Hg distribution in the various size-fractions

Particle size (µm)	Weight (%)	Hg content (ppm)	Hg distribution (%)
-850 +20	11.00	113.9	3.53
-20 +5	4.00	107.6	1.22
-5	85.00	397.4	95.25
Mud	100.00	354.6	100.00

The results obtained by characterisation of the mud shows that the whole sample needs to be treated to meet environmental standards. SEM analysis, Figure 3, carried out with an SEM HITACHI S2500, BSE mode, reveals the presence of metallic mercury as small drops measuring about 5µm.

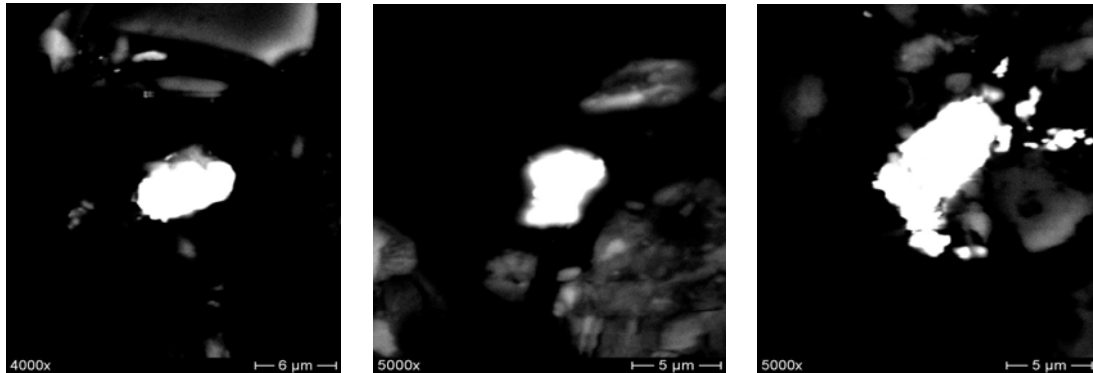


Figure 3. Metallic mercury particles as revealed by SEM (4000x, 5000x, 5000x from left to right)

3. RESULTS AND DISCUSSION

Mercury removal from the mud was carried out utilising a laboratory-scale set-up based on the flow-sheet shown in Figure 4. Tests were carried out in order to assess optimal desorption temperature and roasting time for mud clean-up. Heating to a temperature higher than 600°C was avoided in order to prevent degradation of calcite, as revealed by thermal analysis.

During desorption tests, carried out at various desorption temperatures and roasting times, evaporated mercury was collected by sequential traps containing a solution of KI/HCl. Chemical analyses of all the calcines after roasting shows that a temperature of 400°C and a roasting time of 20min ensures a residual mercury concentration in the calcine of 4.66ppm (namely below the regulatory limit of 5ppm) and 99% mercury removal.

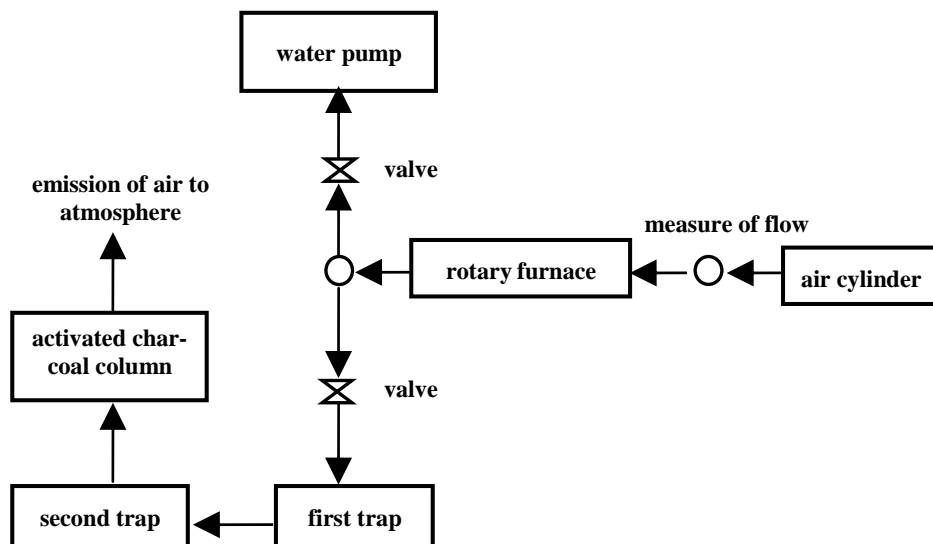


Figure 4. Process flowsheet adopted for mercury desorption from the contaminated mud

Figure 5 shows the isotherms for the residual mercury content in the calcine after roasting as a function of desorption time.

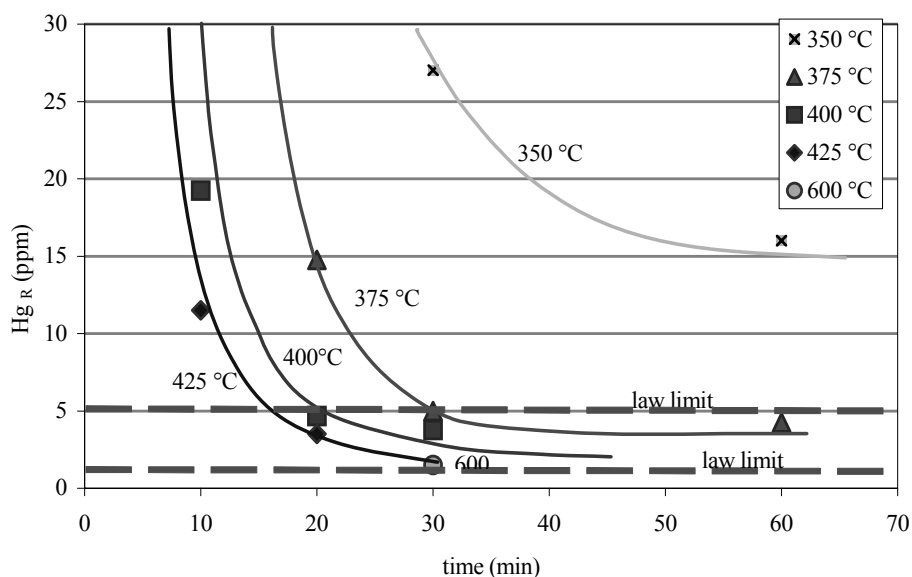


Figure 5. Desorption isotherms for residual mercury content in the calcines (t= time; Hg_R= Hg in the calcines)

Addition of FeS proved to be very profitable as a catalysing media in the presence of HgS, but it does not seem to ensure similar efficiency in treatment of the sampled mud, due to the speciation of Hg in metallic form, without recurrence of the HgS species.

Experimental tests, carried out with the aid of FeS at 300°C, do not indicate any improvement in the decontamination results.

Mercury content reduction to below the previous limit was obtained only after roasting up to 600°C: less than 1.5ppm of mercury occurred in the calcine decomposition of calcite. Consequently it may be supposed that few mercury species were trapped in the carbonate matrix.

The least square method was applied to the results obtained from the experimentation with the aim of finding a regression equation for predicting residual mercury concentration in the calcine at a fixed desorption temperature and roasting time. The method is based on the minimisation of the following expression:

$$e = \sum_i (y_m - y_c)^2 \quad i = 1 \dots n \quad (1)$$

e = measurement deviation

y_m = measured Hg content in the calcine

y_c = calculated Hg content in the calcine

n = number of tests

Various assumptions were made in order to obtain a model approximating to the experiments.

The best regression equation is shown at the top of Figure 6, where the experimental data are plotted with the value predicted by the model.

Negative coefficients of desorption temperature and roasting time in the regression equation express the fact that residual mercury concentration in the calcine is inversely proportional to the increase of these two parameters.

Deviation from data (mercury concentration) coming from the model and data deriving from experiments are plotted in Figure 7.

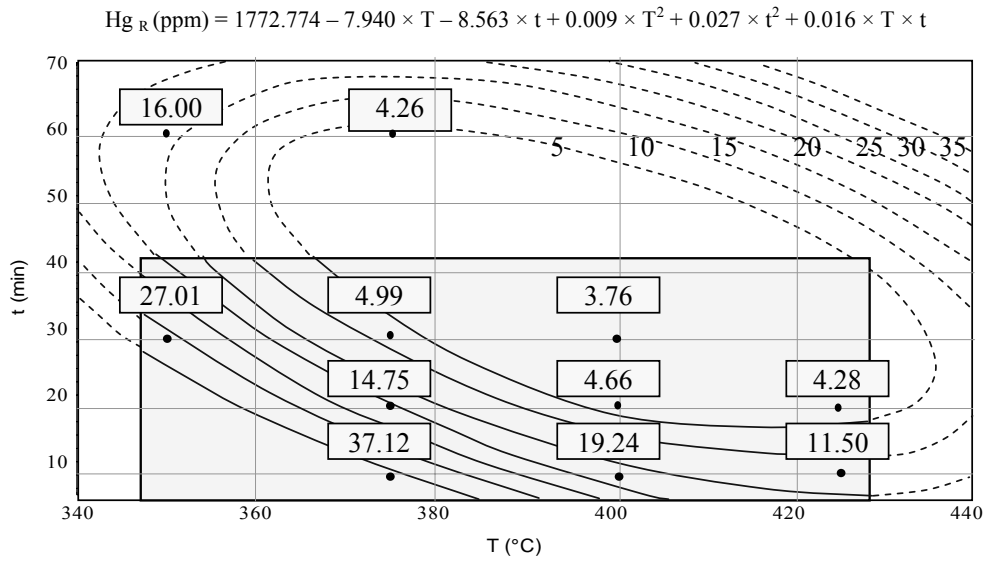


Figure 6. Hg content (ppm) in the calcines versus desorption temperature and roasting time (plot of the model). The coloured area represents the experimental region under study best approximating to the experimental results (Hg_R= Hg in the calcines; T= temperature; t= time)

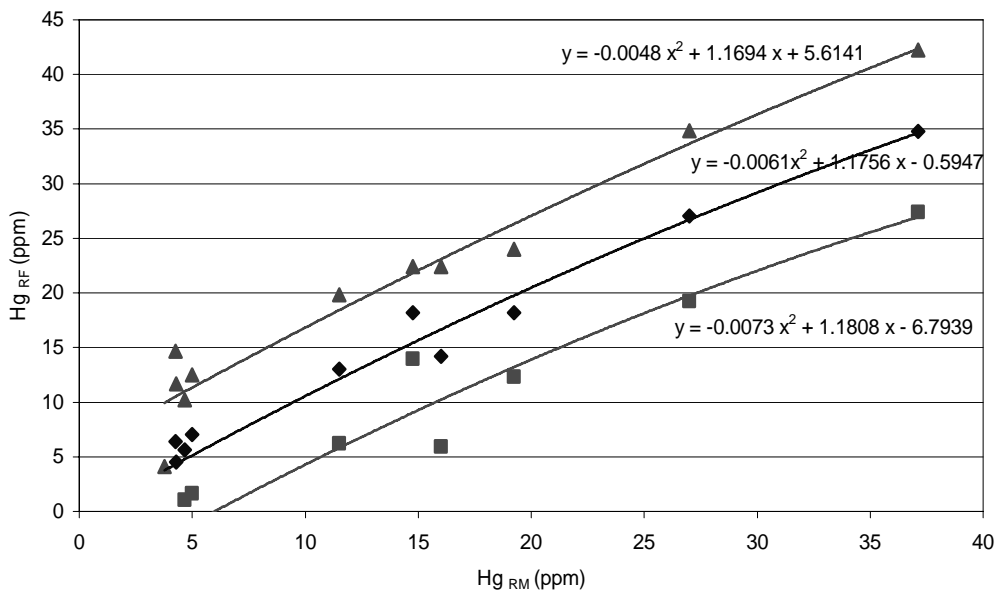


Figure 7. Confidence intervals, within which there is 95% probability that the measured value fits that calculated for the Hg content in the calcines (Hg_{RM}= Hg content measured in calcines; Hg_{RF}= Hg content in the calcines as predicted by model)

The various sections of the laboratory set-up adopted for thermal treatment are shown in Figure 8 which also reports the distribution of mercury condensed therein. Most of the polluting element was condensed out of the furnace and only a small part (about 15%) was recovered in the traps.

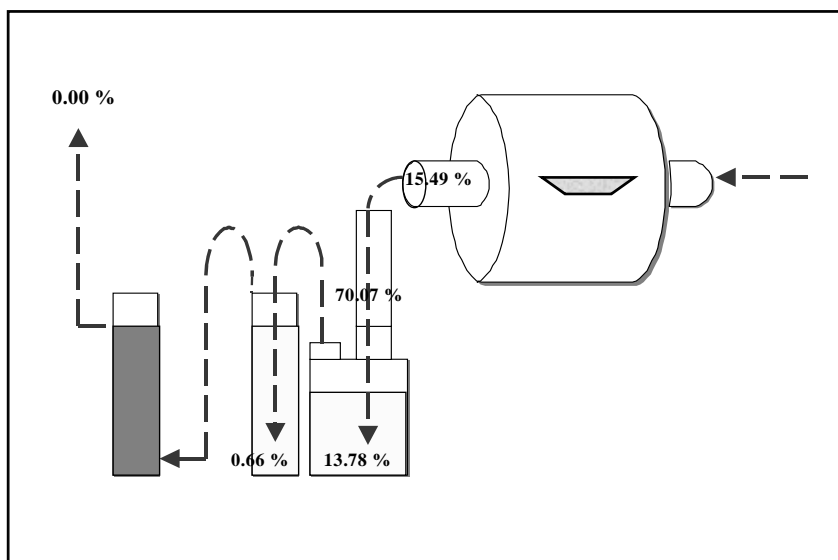


Figure 8. Mercury distribution in the various sections of the laboratory set-up

Mercury mass balance to ascertain the amount of the mercury removed by the mud was calculated by subtracting mercury in the calcine from that in the feed: the results are reported in Table 2.

Table 2
 Mercury extraction in the experimental tests (T = temperature; t = time)

Sample	Feed	Roasting conditions		Computed extraction		Measured extraction Hg _L (%)
	Hg _F (ppm)	T (°C)	t (min)	Hg _R (ppm)	Hg _C (%)	
TRI 28	363.34	375	30	11.44	96.85	
TRI 29	345.50	400	20	17.83	94.84	
TRI 30	343.24	400	30	12.86	96.25	
Total	350.74	≈400	≈30	14.02	96.98	96.12

* Hg extraction (computed) = $Hg_C = [(Hg_F - Hg_R) / Hg_F] \times 100$ = Hg in the feed minus Hg in the calcine divided by Hg in the feed (percentage), Hg extraction (measured) = Hg_L = fraction of total mercury coming from desorption and recovered after washing the traps of the experimental set-up

After purification in the traps, the air leaving the set-up during the roasting tests was monitored with a multifunctional mercury analyser (Lumex mod.RA-915 analyser). The average value of all measurements was 0.000108mg/m³, where 0.05mg/m³ is the regulatory limit for mercury emissions (Ministerial Decree 124/2000). The results obtained by means of the experimental campaign permitted production of a flow-sheet (Figure 9) for mercury decontamination of the mud. The flow-sheet consists of a mercury-removal section and a mercury-abatement section.

Mud is fed to a dryer (120°C), for dewatering, and then processed by thermal treatment for 20 min in a rotary furnace operating at 400°C. The mercury content of the calcine is below the regulatory limit, so it can be returned to the site. Hg-bearing air, coming from the rotary furnace, is collected together with air coming from the dryer (this contains Hg and water vapour before purification). The air is sent to the heat exchanger where it is cooled to condense the mercury. The mercury dusts contained in the air flow have to be treated in a de-dusting device. The counter-current air leaving the heat exchanger can be recirculated to the dryer for drying the mud. Air flow coming from de-dusting is sent to a washing tower and then to an iodate-activated charcoal trap. Exhausted charcoal is sent to landfill. Process water is then subjected to decontamination treatment. The whole of the decontamination system has to be kept under low vacuum to avoid leakage of mercury (10torr). Decontaminated air with an Hg content below the regulatory limit can be released to the atmosphere. Due to the low temperature and the short roasting period needed for decontamination, all the thermal treatment can be carried out using an electric furnace.

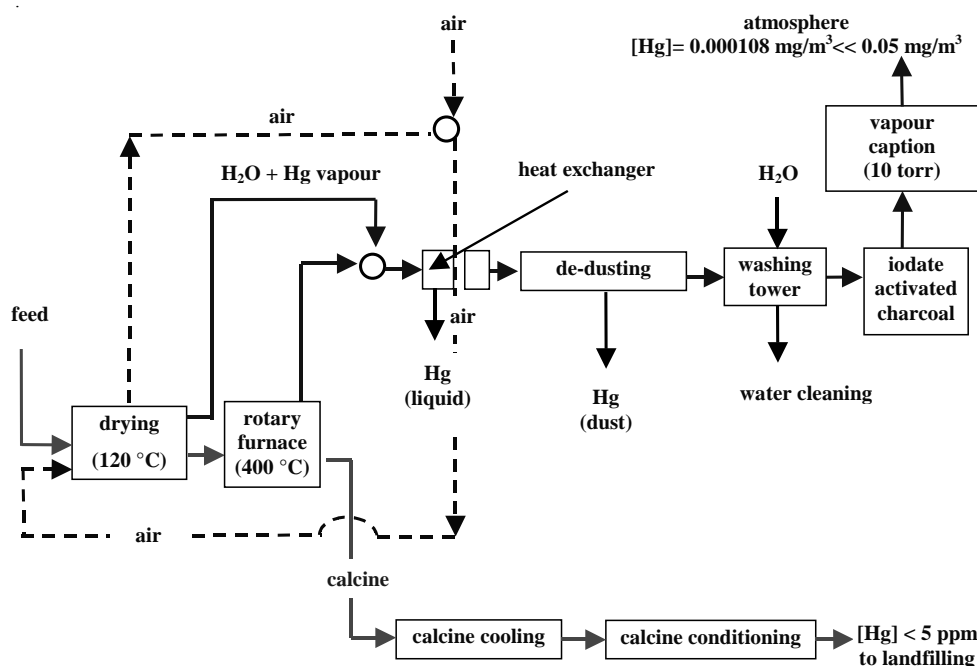


Figure 9. Flowsheet adopted for decontamination of polluted mud

4. CONCLUSIONS

Experiments, carried out on a mercury-polluted mud from a chlor-alkali plant show that a desorption temperature of 400°C and a roasting time of 20min produce a calcine with a mercury concentration below the regulatory limit of 5ppm. Mercury extraction amounts to 99%.

After passing through traps containing an acidic solution of KI, the air leaving the experimental set-up has a mercury concentration well below the regulatory limit for mercury emissions.

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