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Possibilities for reusing the waste from the process of Zn-Pb ore beneficiation

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Abstract. This paper discusses the areas of storage, resources, and granulometric and chemical characteristics of old Zn-Pb tailings stored in heaps in the city of Bytom area. It presents the results of laboratory tests for development of the technological flowsheet for transformation of the material into Zn-Pb sulfide concentrates and the results of trials in an experimental system of the beneficiation flowsheet which was developed. In the further part of the paper, the results of the research work on preparation of the tailings with reduced metal content for further use are presented.

1 Introduction

In years 2015 – 2017 IMN carried out research within the project called "Waste-free technology for processing of the Bytom area heaps with the recovery of concentrates for Zn-Pb production". The project concerned the development of a waste-free technology for processing of the material from old heaps of tailings generated in XX century during operation of beneficiation plant for zinc-lead ores of "Orzeł Biały" mine and smelter. The idea of the project was to develop a technological flowsheet for production of selective or collective sulfide concentrates of zinc and lead out of the tailings and the testing of the remaining material (secondary tailings) for possible use in mining technologies, production of aggregates and fillers, as well as engineering works.

The existing wastes of Zn-Pb ore beneficiation processes in this area could be a valuable raw material for the production of zinc and lead concentrates for ZGH "Bolesław" or HC "Miasteczko Śl" zinc smelters. Due to the large distance to both plants, the optimum method of use would be processing them in a specially designed beneficiation plant located on site.

2 Determination of the volumes of resources and metal content in the examined waste

The main goal of the project was first to identify the currently available waste resources from the examined area and then to develop a flowsheet of waste processing for the intended production of selective or collective concentrates of Zn and Pb. The examination covered four waste heaps: OG/81, OG/ 88, OG/86 and OG/85.

The test material was composed of samples from individual heaps extracted by the drilling. Based on them the detailed inventory of the examined sites was performed. The volume of heaps and the average metal content in them were presented in Table 1.

The presented data indicate that, from an economical point of view, the most interested is heap OG/81, with its resources being approx. 3.173 million tons, which represents 84.8% of the examined resources of waste in the area. The second largest heap is OG/88 with a total waste amount of approx. 330.5 k tons, which is 8.84% of the total resources.

Because of low content of lead in the sulfide form in the range of 0.24% Pb(S), the potential for production of selective Pb concentrates is very limited. Therefore, examination of the flotation process has been performed with the focus on production of collective Zn-Pb concentrates.

3 Determination of the optimum conditions for Zn-Pb collective flotation

The basic parameters of the flotation process covered by the laboratory tests were: feed grain size distribution, amount of added reagents and concentration of solid particles in the feed material.

Preparation of the materials for the flotation trials started with crushing to the grain size of < 2 mm; next, the samples were milled in a wet state in a laboratory rod mill to the grain size of < 0.2 mm, < 0.15 mm and < 0.1 mm. Flotation tests have been performed in a laboratory flotation machine (Mechanobr type) with a cell capacity of 1L. Other flotation parameters were as follows:

- Solid particles concentration in the feed – 200 g in 1 L, 350 g in 1 L, 500 g in 1 L
- Doses of $CuSO_4$ – 350 g/t; Hostaflot X 23 – 20 g/t, 25 g/t, 30 g/t; Amyl xanthate – 25 g/t, 30

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g/t, 35 g/t; Ethyl xanthate – 15 g/t, 20 g/t, 25 g/t; Corflot – 15 g/t
- Flotation time – 15 minutes (3 min + 5 min + 7 min)

During the process of flotation, three froth products were taken: the first one after 3 minutes of flotation, the second one after 8 minutes of flotation and the third one after 15 minutes of flotation. The froth products and waste product (tailings left in the flotation cell) were dried and then weighed to determine their yield. Next, the samples were analyzed to determine the content of Zn, Pb and Fe.

Based on the obtained mass and metal content in individual products, flotation process mass balances were made for zinc, lead and iron. Based on the balance data, a beneficiation capability curve for the analyzed metal as the recovery versus its content in the froth product was presented. Pictures 1 –3 present zinc beneficiation curves depending on the feed material grain distribution, solid particles concentration in the feed and the amount of collectors added to the flotation, for the example, of the largest heap OG/81.

With the tailings from heap OG/85, completely negative flotation results were obtained in the test conditions, as the froth products brought practically no zinc beneficiation. Due to the lack of real possibilities of enrichment of the material with the flotation method, it was excluded from further tests.

In terms of size distribution, the flotation process is optimal when the waste is milled down to < 0.15 mm. Finer milling of the feed material does not lead to a significant increase of the zinc recovery, while reduction of zinc content in the froth product is observed, which results mainly from mechanical transfer of the finest grains. The second parameter which was tested was the concentration of solid particles in the flotation feed. The optimum value is approx. 350 g in 1 L. Although flotation at the lowest concentration allows to obtain froth products with higher zinc content, it reduces the recovery. The last parameter examined was the amount of collectors added to the flotation. As shown by the presented beneficiation curves (fig. 3.3), the optimum amount of added collectors in this case is approx. 75 g/t (X 23 - 25 g/t + KXamyl- 30 g/t and KXetyl + 20 g/t). Increasing the dose to 90 g/t does not lead to a significant increase in the zinc recovery, while a reduction in the amount of zinc in the froth product is observed. The results also show that in the process of the flotation, an important factor can be the amount of the finest particles in the feed, which can be a major obstacle for obtaining commercial collective Zn-Pb concentrates.

Table 1. Volumes of resources and metal content in the examined heaps of tailings.

	Heap OG/81	Heap OG/86	Heap OG/86	Heap OG/85	Total
Area, ha	11.685	1.038	0.977	0.923	**14.623**
Cubic volume, m^3	1 670 000	171 270	47 288	76 000	**1 964 558**
Bulk density, t/m^3	1.90	1.93	1.94	1.94	**1.91**
Resources, t	3 173 000	330 551	88 901	147 440	**3 798 431**
Zn, %	4.01	5.16	5.18	7.30	**4.27**
Zn(O), %	2.06	2.69	2.70	4.22	**2.22**
Zn(S), %	1.95	2.47	2.48	3.08	**2.05**
Pb, %	0.81	1.25	0.93	1.21	**0.87**
Pb(O), %	0.56	0.93	0.53	0.69	**0.60**
Pb(S), %	0.24	0.31	0.39	0.52	**0.27**
Fe, %	9.38	11.50	7.93	18.81	**9.90**

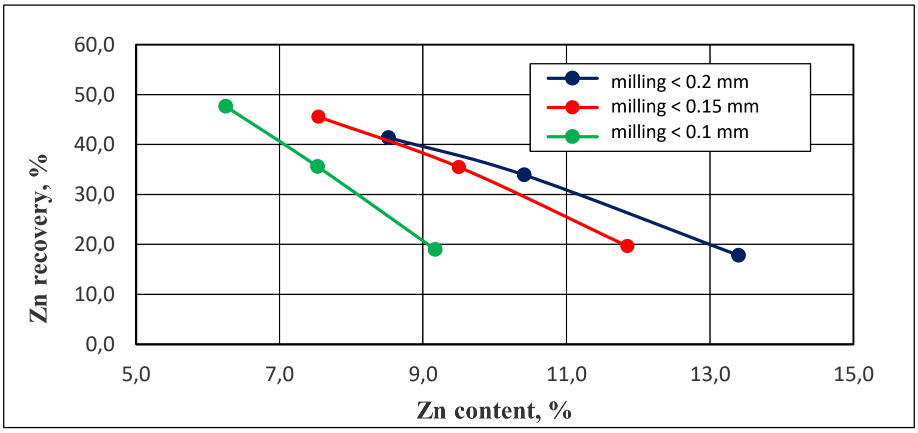

Fig. 1. Heap OG/81. Zinc recovery depending on its content in the froth product at different grain distributions of the feed for flotation.

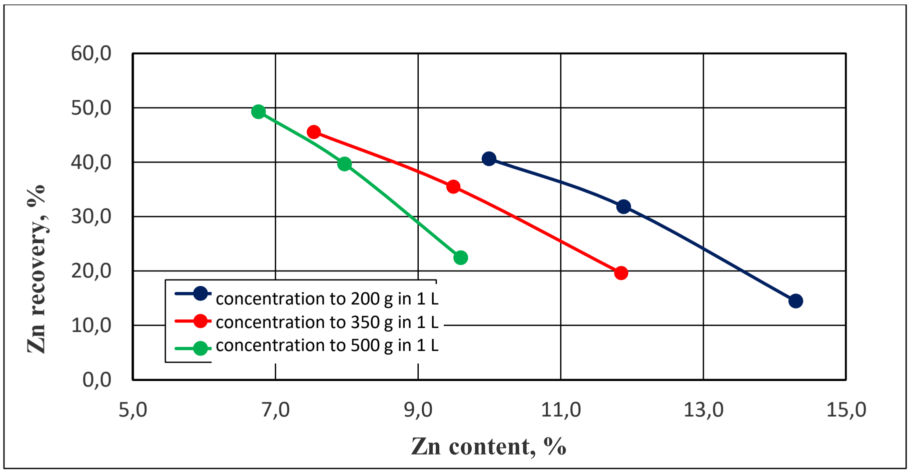

Fig. 2. Heap OG/81. Zinc recovery depending on its content in the froth product at various solid particles concentration in the feed for flotation.

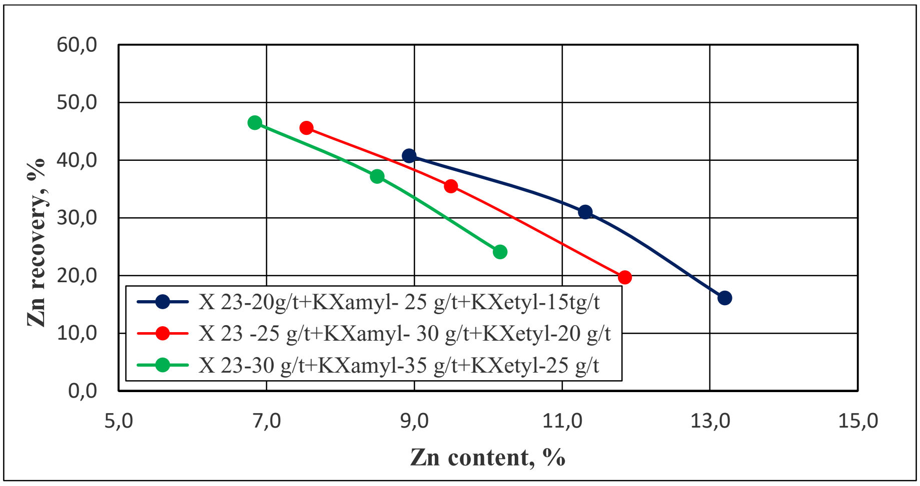

Fig. 3. Heap OG/81. Zinc recovery depending on its content in the froth product at different doses of flotation collectors.

4. Flotation testing in a flowsheet with cleaning flotation

The objective of this stage of testing was to determine the conditions which would enable the production of commercial Zn-Pb concentrates containing Zn+Pb > 50%. The final product requires a series of cleaning flotation trials according to an adequate beneficiation flowsheet.
In the first case, the simplest beneficiation flowsheet, in which waste flotation was split into two stages covering the rougher and scavenger flotation of Zn-Pb is tested. The froth product from the rougher flotation showing the highest content of zinc is fed to the two-stage cleaning flotation, where the final product will be obtained. The froth product from the scavenger flotation showing a relatively low content of zinc is returned to the start of the rougher flotation. This flotation is also fed with the waste product from the first cleaning flotation, while the waste product of the second cleaning flotation returns to the preceding operation, i.e. the first stage of cleaning.

Mass balances of the flotation trials in this flowsheet are presented in Table 2.

The presented balance data show that in this flowsheet the collective concentrates with the required content of Zn+Pb > 50% cannot be obtained. Their amount is only 36.44% to 42.6%. This flowsheet shows a high contribution of technological reverts which are fed to the start of the rougher flotation, being 20% to approx. 32.5% of the fresh feed.

5 Testing in a flowsheet with a separate flotation of the mud fraction

Obtaining commercial concentrates of zinc and lead containing > 50% Zn+Pb would require the introduction of more cleaning stages. In practice, such a solution is disadvantageous, as it leads to a significant reduction in the recovery of metals in the concentrate. It is believed that the reason for poor beneficiation in this flowsheet can be the high content of the finest grains in the flotation feed.

In order to check if these grains have such a high influence on the beneficiation parameters, flotation trials were performed in the most extended beneficiation flowsheet covering the classification of the flotation feed

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into mud fraction and sand fraction, followed by separate flotation cycles.

In this case, the samples of waste milled down to <0.15 mm were separated in a laboratory hydrocyclone, with a diameter of 30 mm, into mud and sand fractions, where mass outputs of the overflow fractions in the range of 28 – 33% were obtained. The mud fraction was processed in flotation with the reduced concentration of solids at 140 – 160 g in 1 L, a higher dose of collectors and the addition of sodium silicate as the depressor of the finest grains of the gangue. For the sand fraction, flotation conditions were not changed.

Results of tests with a separate flotation run for the mud fraction are presented on fig. 4 as zinc beneficiation curves. For comparison, the figure also includes zinc beneficiation curves for the feed with a solid particles concentration of 350 g in 1 L which were obtained in conditions without a separate mud fraction flotation cycle. The comparison of beneficiation curves show that in all cases there was a significant improvement of zinc flotation results with a separate mud fraction flotation cycle. The significant improvement of Zn content in the froth product and the increase of Zn recovery were also observed. So, in order to obtain qualified collective concentrates containing > 50% Zn-Pb from the tested wastes it will be necessary to expand the technological flowsheet for beneficiation with the mud fraction flotation system.

Table 2. Mass balances of the beneficiation of waste from the Bytom area in a flowsheet with cleaning flotation.

Product	Yield	Content, %			Recovery, %		
	%	Zn	Pb	Fe	Zn	Pb	Fe
Heap OG/81							
Feed	100.00	3.96	0.97	9.62	100.00	100.00	100.00
Conc. Zn-Pb	3.64	35.12	1.32	18.40	32.27	4.95	6.96
Waste	96.36	2.78	0.96	9.29	67.73	95.05	93.04
Heap OG/86							
Feed	100.00	5.18	0.94	8.05	100.00	100.00	100.00
Conc. Zn-Pb	3.86	41.28	1.31	13.25	30.73	5.37	6.35
Waste	96.14	3.73	0.93	7.84	69.27	94.63	93.65
Heap OG/88							
Feed	100.00	5.21	1.18	11.65	100.00	100.00	100.00
Conc. Zn-Pb	4.35	37.64	1.54	15.20	31.44	5.68	5.68
Waste	95.65	3.73	1.16	11.49	68.56	94.32	94.32

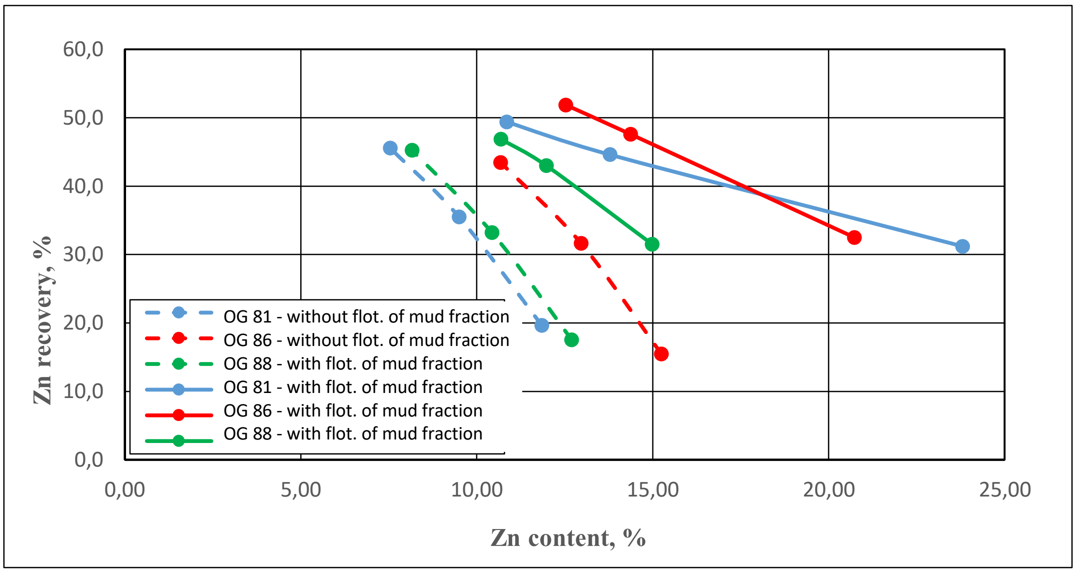

Fig. 4. Relation of zinc recovery to Zn content in the froth product in flotation with and without separate mud fraction flotation cycles.

6 Verification of the developed beneficiation flowsheet in an experimental system

The beneficiation flowsheet developed on the laboratory scale was verified in an experimental system in continuous operation in conditions representing industrial production. During the trials, it was confirmed that in order to reduce the amount of returned material to the start of the rougher flotation of the mud fraction, it would be beneficial to implement an additional operation, i.e. separating flotation performed at a higher pH of the suspension, to which depleted froth products from the stages of the scavenger flotation of the mud and sand fractions, containing large amounts of marcasite will be fed. In this case, the mud fraction rougher flotation will be fed only with the returned froth product from the separating flotation enriched with zinc, while the cell product containing mainly marcasite will be fed directly to the final waste stream. This operation is very important in the beneficiation of materials containing high amounts of sulfide iron minerals, as it reduces the volume of their revert to the start of flotation.

Mass balances of the flotations performed are presented in Table 3. Compared to the results obtained in the previous flowsheet, the introduction of the separating flotation enabled higher Zn content in the concentrate and a slight increase of Zn recovery in the concentrate. This is particularly seen in waste from heap OG/88, which contains the highest amounts of sulfide iron minerals. In this case, the content of zinc in the concentrate increased from 48.6% to 50.8% Zn and its recovery increased from 31.5% to 32.16%.

Table 3. Mass balances of the beneficiation tests in the experimental system.

Heap OG/81							
Product	**Yield**	**Content, %**			**Recovery, %**		
	%	**Zn**	**Pb**	**Fe**	**Zn**	**Pb**	**Fe**
Feed	100.00	3.93	0.93	8.43	100.00	100.00	100.00
Concentrate	**2.71**	**51.60**	**1.23**	**10.30**	**35.64**	**3.60**	**3.32**
Waste	97.29	2.60	0.92	8.38	64.36	96.40	96.68
Heap OG/86							
Feed	100.00	5.19	0.94	8.09	100.00	100.00	100.00
Concentrate	**3.25**	**53.26**	**1.83**	**7.62**	**33.38**	**6.33**	**3.06**
Waste	96.75	3.57	0.91	8.11	66.62	93.67	96.94
Heap OG/88							
Product	**Yield**	**Content, %**			**Output. %**		
	%	**Zn**	**Pb**	**Fe**	**Zn**	**Pb**	**Fe**
Feed	100.00	5.21	1.19	11.71	100.00	100.00	100.00
Concentrate	**3.30**	**50.82**	**1.64**	**9.35**	**32.16**	**4.54**	**2.63**
Waste	96.70	3.65	1.17	11.79	67.84	95.46	97.37

Table 4. Mass balances of the waste thickening after flotation of tailings from heaps with the use of a double classification system in hydrocyclones.

Product	**Yield %**	**Qs, kg/min**	**V l/min**	**Weight 1 l g**	**Density of solids g/l**
Flotation waste	100.00	15.00	62.50	1160.0	240.0
HC discharge 2nd stage of discharge classification	77.76	11.66	7.68	2012.4	1518.6
Discharge of the lamella clarifier	21.92	3.29	6.26	1350.0	525.0
Overflow of the lamella clarifier	**0.32**	**0.05**	**48.56**	**1000.7**	**1.0**
HC discharge 2nd stage of discharge classification + discharge of the lamella clarifier	**99.68**	**14.95**	**13.94**	**1714.9**	**1072.3**

7 Tests of the process of thickening and dewatering of flotation tailings

Prior to its further use, the waste product ('secondary tailings') requires first thickening and, if necessary, dewatering, if it is used for ground leveling and similar purposes. The easiest way to prepare the thickened waste would be to feed it to the Dorr settler, where the discharged product would make a material ready for further applications or for dewatering, while the clarified water obtained as the overflow product would be returned to the flotation circuit.

The waste which was tested shows a very low sedimentation rate, which results from the significant presence of the finest grains <15μm. The average sedimentation rate is $v = 1.884 \cdot 10^{-5}$m/s, which results in 6.8 cm thick layer of clarified water in 1 hour. With the assumed quantity of processed waste being 42.3 t/h, the required surface area of clarification would be 2540.0 m^2. For this surface area, the minimum diameter of Dorr settler is D = 56.9 m. From a technical point of view, such a high diameter is unacceptable. To solve this problem, trials with thickened waste in an extended flowsheet with the use of hydrocyclones were performed in the experimental system.

The first stage of classification occurs in the hydrocyclone, the overflow product of which is fed to the second stage of classification in the hydrocyclone**.** The overflow product from this hydrocyclone with solids at approx. 60 g/l is thickened in a lamella clarifier, where clarified circulating water and thickened sludge, which is the second component of the thickened waste, are produced. The discharge product from the first stage of classification is subject to secondary thickening in the hydrocyclone. The discharge product from this stage is a thickened final product and together with the sludge of the lamella clarifier it represents the thickened material intended for further use.

The mass balance of the process of waste thickening in this flowsheet is presented in Table 4.

In the last stage, dewatering trials with the thickened waste were performed.This results from the need to prepare them in a form that allows safe road transportation if they are to be used as materials for ground leveling. The examination covered the testing of thickened waste from the experimental system with a solids content of approx. 1000 g/dm^3.

The tests of suspension filtration were performed in a laboratory pressure type filter press with plate dimensions 0.63 x 0.63 m and 20 mm thick filtering chamber. Results of the completed trials were as follows:

1. The sludge shows a lump structure with a moisture content of 17 – 21% H_2O,
2. Specific density of the cake in a wet state is 2.2 kg/dm^3.

This data allows us to define the volume of filter chambers for the target plant with the capacity of 41- 42 t/h and initial thickening of approx. 1000 g/dm^3 with the following parameters:

1. Filtration time – 20 minutes
2. Number of cycles per hour – 3

The calculated volume of filtering chambers for the obtained moisture levels is 5 500 dm^3 to 6 500 dm^3.

8 Conclusions

1. Based on the geological drillings, a detailed inventory of the examined heaps of tailings generated in Zn-Pb ore beneficiation in the Bytom area was made. The total waste resources are 3 798 431 tons and the average metal content is: Zn – 4.27%, Zn(O) - 2.22%, Zn(S) - 2.05 5%, Pb –0.87%, Pb(O) – 0.87%, Pb(S) – 0.27%, Fe – 9.9%.
2. Among the three examined beneficiation flowsheets, only the one with a separate flotation for the mud fraction and the segregating flotation brings collective concentrates with the required content of Zn+Pb. For the waste from heap OG/81 containing 3.93% Zn, the obtained concentrate contained 51.6% Zn and 1.23% Pb with a zinc recovery of 35.61%, for the waste from heap OG/88 containing 5.2% Zn, the obtained concentrate contained 50.82% Zn and 1.64% Pb with a zinc recovery of 32.2%, for the waste from heap OG/86 containing 5.2% Zn, the obtained concentrate contained 53.26% Zn and 1.83% Pb with a zinc recovery of 33,4%.
3. Implementation into industrial practice of the waste-free technology of processing of Zn-Pb wastes from the Bytom area, i.e. application of the waste for production of sulfide concentrates of zinc and lead and then using the generated secondary tailings with depleted zinc in engineering works, would require development of an efficient method of thickening and dewatering to ensure safe transportation to the destination.
4. The completed tests show that due to the unfavorable size distribution, i.e. presence of approx. 66% of the waste in the finest grain category < 0.036 mm, the process of waste thickening in natural conditions is ineffective with its low sedimentation rates. This problem was solved by application of a system with two stages of classification in hydrocyclones, plus a lamella clarifier for thickening the overflow product from the hydrocyclone of the 2nd stage. This system delivers thickened waste material and clarified circulating water being the overflow product of the lamella clarifier. After treatment of the feed with solids thickened to 240 g in 1L a final product with solids thickened to 1070 g in 1L and circulating water with solids content < 1 g in 1 L are produced.
5. The performed test of filtrations of the thickened waste product confirmed the possibility of product dewatering to an average moisture of approx. 19% H2O. For the target system of 41- 42 t/h capacity and initial suspension density of 1000 g/dm^3, the calculated volume of filtering chambers is 5500 dm^3 to 6 500 dm^3.

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