Process for Stabilization of Heavy Metals From Solid Waste Resulting in the Process of Acid Mining Water Treatment

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Abstract. The technology and the installation of acid mine water treatment by bioaccumulation, is realized in three distinct stages, namely: the primary stage, consisting of raw water capture, treatment with neutralizing and coagulating chemical reagents, solid phase settling and sludge treatment, [I, II , IV, V], the secondary stage, consisting in the removal of heavy metals and the neutralization of acidity by passing the effluent of the first stage, through a battery of phytoextraction cells, [III],using for this purpose truncated cells. In the tertiary stage, the stabilization of heavy metals in the thickened clearing and the aerial part of the sedge takes place.

1 Description of the invention

The technological flow in figure no. 1 is characterized by the fact that, for the treatment of acid mine waters, a catchments is provided (I), which is a bicameral reinforced concrete construction, located perpendicular to the water flow (1). In the first room - catchments chimney - (2), provided at the front and in the ceiling with lamellar grilles or stamped sheet metal with 10 mm mesh (3), which retain the coarse material bodies, the entire amount of raw waste water accumulates. In the second chamber (4) - of the pumps - two centrifugal pumps (5) (one spare) are mounted, which discharge the raw water into the vertical decanter (II). The reagent processing and dosing station can also be arranged in this room (6) [1, 2].

The vertical decanters with fluidized bed (II) are cylindrical in shape, through which water flows from the bottom up. Vertical decanters are used in places where there is not enough space and only in the case of small installations (up to about 15,000 m^3/day and 625 m^3/h respectively) at a continuous operation of 24 hours a day [1, 2].

The raw water - the influent - discharged by the centrifugal pump (5) reaches the supply tube of the decanter (7) which communicates with the central tube (8) sunk to a depth H, so that meeting the conical deflector to form an upward radial current with a velocity (u) lower than the sedimentation rate (v_o) determined experimentally by sedimentation tests, thus respecting in each section the condition $u \leq v_o$. For this purpose, the coagulating and

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neutralizing reagent, calcium hydroxide, is dosed in the raw water flow, thus ensuring, until leaving the central tube, the mixing of the reagent with the raw water.

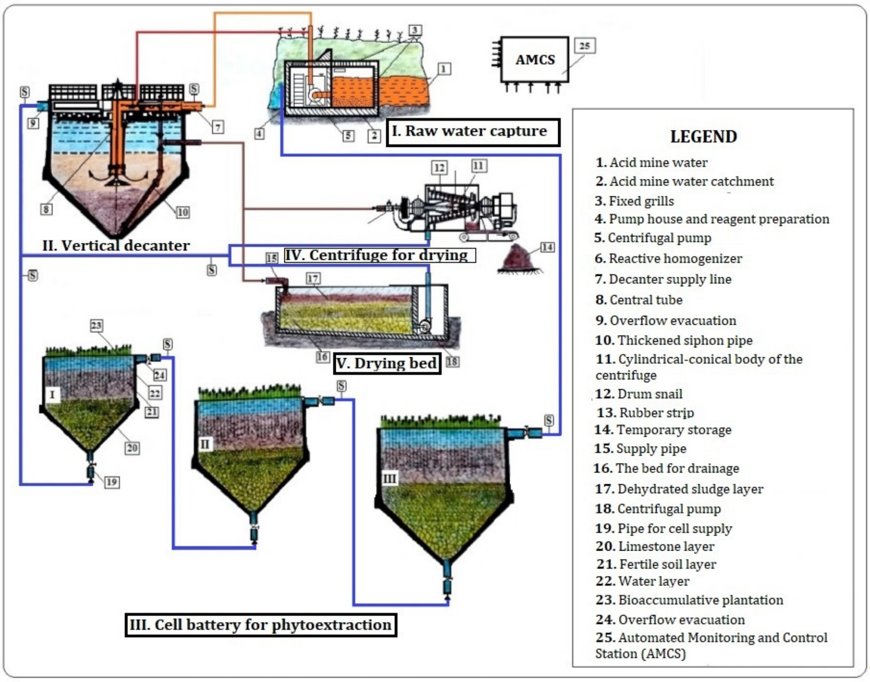

Fig. 1. Technological flow of acid mine water treatment.

Under these conditions, all the distinct or flocculated particles, characterized by the limiting velocity $v_o > u$ will settle in the counter current, accumulating at the base of the decanter, an area called the mud funnel, forming the thickened product. All particles with velocity v0 <u will be entrained in the overflow decanter in the form of clarity. The discrete or flocculated particles with $v_o = u$ will form a fluidized layer (bed), in a certain dynamic equilibrium, which constitutes a filter in the way of the ascending particles and flocculates, thus ensuring an advanced degree of clarification. Of course, because of this the fluidized bed will be difficult and periodically a layer will break from it that will accumulate in the mud funnel. The clarified water is collected in a peripheral gutter - overflow gutter (9), and the deposits are collected in the mud funnel. Deposits are discharged continuously or intermittently through a siphon line (10) [1, 2].

During normal and continuous operation the two cleaning products must be removed continuously. Thus, the clarification accumulated in the overflow of the decanter constitutes the supply of the phytoextraction stage, and the thickening is subjected to an advanced drying operation either in drying centrifuges or on drying platforms.

In both cases, the dried material to the humidity that allows its safe transport is stored temporarily in a specially arranged deposit, and the leachate is recirculated in the supply of the first phytoextraction cell.

2. Mechanical dehydration by centrifugation

In decontamination of water in order to dry the thickeners, decanter centrifuges with horizontal axis, with continuous operation (IV) are usually used.

In principle, they consist of a rotating cylindrical-conical body (11) in which it rotates, in turn, in the same direction, but with a slightly lower speed - a worm drum (12). The thickener of the decanter is inserted axially and is projected, under the action of centrifugal forces towards the inner face of the centrifuge body (11). The solids deposited on this wall are scraped and pushed by the worm body (12) towards the end of the conical area of the centrifuge body, evacuating continuously. The desiccant is continuously taken up by the rubber band (13) and temporarily stored in a specially arranged warehouse (14).

Leakage (clarification) due to the content of colloidal suspensions and heavy metals joins with the clarification of the vertical decanter (II) and together is the supply of the first stage of phytoextraction (III) [1, 2].

3. Natural dehydration of the thickener on drying platforms

It is widely used, given its simplicity of construction and low operating cost.

When the quality of the thickener does not require special storage conditions and the field conditions offer this possibility, natural dehydration on drying beds is preferred.

Drying platforms (V) are dammed land surfaces in which sludge is stored. The dimensions of the drying platforms are chosen according to the method adopted for the evacuation of dehydrated sludge. When evacuating the sludge is done manually, the width of the bed should not exceed 4 m; evacuation by mechanized means allows a width of up to 20 m. The length of the drying platforms is mainly determined by the slope of the ground and must not exceed 50 m. The platforms can be placed on a permeable or impermeable base layer. The permeable drainage layer is made of slag, gravel or crushed stone with a thickness of 0.2-0.3 m (the supporting layer), over which is placed a finer layer of sand or gravel, with a thickness of 0.2 - 0.6 m. The drainage pipes for collecting leachate are buried in the support layer [1, 2].

The thickness of the sludge layer that is sent to the beds depends on the characteristics of the material and the climate of the respective area. In general, a height of about 0.20 m is recommended for a temperate climate.

The thickening of the vertical decanter is fed and dispersed by means of the pipe (15) upstream of the drying bed in a thin layer evenly distributed (17) over the drainage bed (16) consisting of successive layers of gravel, with controlled grain size descending from the bottom up and a layer of fine sand. The drained leachate is continuously discharged with the centrifugal pump (18) and combined with the clarification of the vertical decanter, constituting the supply of the first phytoextraction stage [1, 2].

The dehydrated sludge is evacuated mechanically and transported to specially arranged landfills.

Determining the duration of sludge dehydration on drying platforms requires knowledge of the physico-chemical properties of the sludge and the climatic regime of the area. In general, in temperate climates, the duration of dehydration is between 40 and 100 days, which means that, in total, you can count on a thickness of mud that spreads on the platform of 1.5 - 2.0 m per year, respectively a productivity of 80 - 100 kg dry matter/m^2 and year.

4. Phytoextraction of heavy metals

The clarified and neutralized water together with the centrifuge leak and / or the leaching of the drying bed constitutes the supply of the phytoextraction battery (III) composed of three biosorption and phytoextraction cells.

The respective volume of the surface of each cell increases progressively from feeding to evacuation, thus achieving a decrease in the ascending speed of the limestone and fertile soil layers, which support the vegetation with heavy metal accumulating properties.

A phytoextraction cell is characterized in that, in order to fulfill its biosorption function, it consists of a frustoconical vessel with a small base at the bottom in which the influent penetrates at the bottom (19) so as to pass through the gaps created by the granules in the limestone bed (20), arranged in three successive layers, in descending order of the size of the granules, at a low speed, which allows ion exchange, pH regulation and retention of heavy metal ions. Above the limestone bed is the biological layer consisting of fertile soil (21) and a plantation of bioaccumulating plants (23). The overflow of each biosorption cell (24) is the supply of the next cell, in which the process of neutralization and phytoextraction continues, and finally purified water is obtained which can be discharged in full sanitation into the emissary, downstream of the capture station [1, 2].

The plant tested for the phytoextraction of heavy metals from acid mine waters and with a high content of heavy metals, according to the invention, is "sedge" with the following properties:

The sedge is a plant over 50 cm tall. It has a very long root, with numerous thin and 2-3 mm long branches, which gives it a good anchorage in the sandy soil. The stem is triangular and hard, the leaves grow vertically, are over 10 cm long but very narrow, dark green, with basal brown sheaths. The inflorescences are conical in shape, 3-8 cm long, in light brown shades. The fruits are in the shape of achenes. The flowering period is from June to September.

It is a perennial plant that grows on sandy and acid soils. It prefers moist, partially shaded soil and is sensitive to pests and diseases. It is also known as the sowar, has the scientific name of *Carex arenaria* and is part of the *Cyperaceae* family. In the natural environment there are about 500 species of sedge belonging to the genus *Carex* and which includes *Carex nigra*, a species used in biosorption cells in the experiment.

As the rate of propagation and development of this plant is high, the aerial part is periodically harvested and subjected to controlled incineration operations and / or recovery of useful elements.

In order to control the supply flow of the complex treatment plant as well as its quality, on the one hand and the effluent quality of each phytoextraction cell, on the other hand, sensors [S] are placed in the key points of the flow with the possibility of measuring pH values turbidity and conductivity, the parameters that give an overview of the quality of the treatment process. The data taken by the sensors are processed in the computerized process analysis, monitoring and control station (25). Depending on the quality of the effluent, all the factors influencing the process, the supply flow, respectively the retention time, the specific consumption of reagents, etc. are regulated.

The tests performed in continuous flow in the micropilot installation (figure 2), which fully respect the hydrodynamic principle and the technological flow described above. Physico-chemical analyzes performed on samples taken from influent, effluent and sediment, as well as stereomicroscopic determinations on the structure of plant tissues, demonstrated the veracity of the proposed solution and the high purification efficiency in the two stages. Thus, the separation efficiency of mineral suspensions increases from 85% by settling to 99% by biofilters, the pH increases from values of 3-4 as raw water has to 6.5-7 by settling and to 8 in the battery effluent of phytoextraction. Referring to the heavy metals Pb, Fe, Cu, Zn, Co, Cr, the results of the experiments showed that it is possible to reach purification efficiencies of 99.5%, with strict compliance with the quality conditions imposed on waters discharged into natural receptors.

The tests carried out in continuous flow in the micropilot installation, the physico-chemical analyzes carried out on samples taken from the influent, effluent and sediment, as well as from the ash resulting from the incineration of the sedge, illustrated in the table no. 1, on the one hand, and the calorific value Dry sludge, on the other hand, has led to the choice of the most viable processing chain for this secondary waste.

For normal and continuous operation, the phytoextraction plant must contain two parallel lines: one in operation and one in preparation and revegetation. Observations made in vegetation vessels on the growth rate of sedge showed that it reaches maturity (height of 80-90 cm) in four months. Under these conditions, in one year, three cycles of purification and harvesting of sedges are carried out.

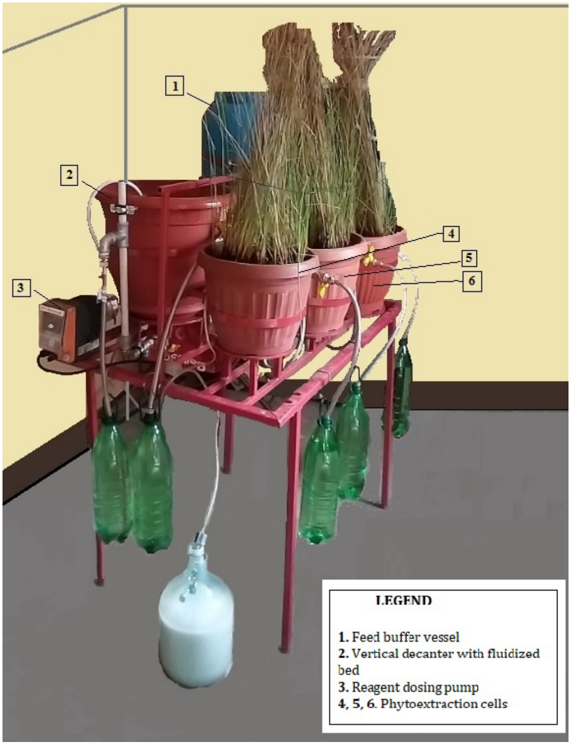

Fig. 2. Experimental plant for the treatment of acid mine water by bioaccumulation.

The recommendation is that the sedge planted in the phytoextraction cells come from the banks of the stream, whose water is treated because it is adapted to soil and environmental conditions or sedge crops can be created to feed the phytoextraction cells throughout the year.

At an industrial flow of influence of 400 m^3/h, the total surface of the phytoextraction cells is 800 m^2 and for a planting density of 4400 yarn of sedge/m^2 results a quantity of biomass of 9.5 t/ha dry matter, which by incineration releases between 13- 6 GJ/t calorific value, depending on humidity.

Analyzing the data in the table 1, it results that the thickening of the decanter decanted by centrifugation and / or on drying platforms, falls within the quality conditions of the soils for less sensitive types of uses, except for the sulphate quality parameter. Sulphates ions are blocked in the form of calcium sulphate (gypsum) given that the coagulant and neutralizing reagent used in the settling phase is $Ca(OH)_2$ (lime milk). Under these conditions, the sediment obtained is sandy and stable and can be deposited in any deposit authorized or used in agriculture as an ameliorator for basic soils with sulphur deficiencies, or in cement plants for mixing with cement clinker.

With regard to the ash obtained from the incineration of the aerial part of the harvested sedge, it is observed that there are flagrant exceedances of the maximum permissible contents provided by the regulations in force for storage, namely: sulphates 182 count of times, Zn 2.14 count of times, Pb 2.6 count of times and Co 3.29 count of times, on the one hand, but at the same time are below the minimum limits for recovery, on the other hand and consequently fall into the category of hazardous waste and must be treated as such.

Mixing the two wastes does not solve the problem but on the contrary makes their management more difficult.

Table 1. Physico-chemical analyzes carried out on samples taken from the influent, effluent and sediment, as well as from the ash resulting from the incineration of the sedge.

Quality indicators	Contents of pollutants in solid treatment products		Medium content in the mixture [mg/kg]	Permitted values Ord. 756/1997 [mg/kg]	Exceedances compared to Ord.756 [count of times]	Accumulation capacity in sedge [%]
	Thickened decanter [mg/kg]	Ashes from the sedge [mg/kg]				
Sulphates	186 000	913 000	539 650	5 000	108	18,10
Total irons	9 900	34 300	19 642	It is not standardized	It is not standardized	93,63
Zinc	530	1 500	873	700	1,247	94,73
Copper	18,00	130,00	83,27	250	-	90,90
Lead	2,9	650	635	250	2,54	100,00
Crom total	2,1	30,8	23,25	300	-	74,00
Cobalt	5,80	329	301	100	3,01	98,25
Total	196 459	949 940	561 207			
Total no sulfates	10 459	36 940	21 557			
Total No irons	559	2640	1915			

As we are dealing with two distinct wastes, the chronological order of the operations regarding their management is presented in the framework scheme from figure 3.

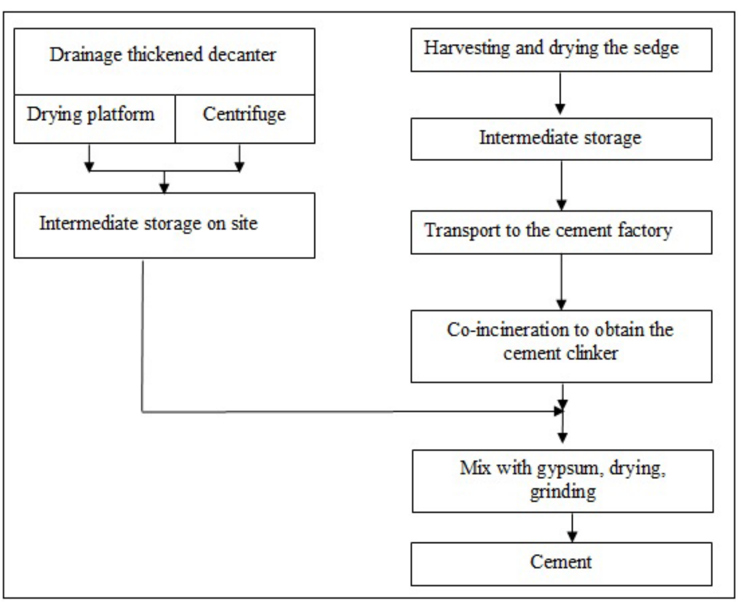

Fig. 3. Framework scheme for solid waste management.

5. Conclusions

The present invention relates to a process for stabilizing heavy metals by co-incineration in cement plants.

The acceptance of waste for co-incineration at cement plants is conditioned by some quality conditions. Comparing these conditions with the quality of the sedge, we notice that it is suitable for co-incineration, being the most economical and safe method for stabilizing heavy metals.

Also to obtain Portland cement, the cement clinker is mixed with a certain amount of gypsum, or the cakes obtained by drying the thickened decanter with a fluidized bed, have high gypsum content and are therefore suitable for mixing.

References

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