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TREATMENT OF PHOSPHORIC ACID SLUDGE FOR RARE EARTHS RECOVERY III: COMPARISON OF SAWDUST FILTER AID AS BODY FEED WITH PRE-COATING

Extra fine sawdust has been utilized as a filter aid for the filtration of the phosphoric acid sludge and recovery of Rare Earth Elements (REE). Results show that the addition of sawdust as a filter aid enhances the filtration in terms of solid residue retained and the quality of either the recovered acid when applied as a pre-coat or a body feed. It was found that an increase of sawdust dosage above 0.5% reduced REE distribution in the final solid residue with a slight increase in the rate of filtration up to 1%. Application of sawdust as a pre-coat resulted in a final dried solid product containing less phosphorus. This study showed that sawdust could be employed as a low-cost commercial filter aid for treatment of the phosphoric acid sludge for recovery of REE, as well as the phosphoric acid value.

Keywords: *Phosphoric acid sludge, sawdust, filter aids, rare earths elements.*
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Introduction

Filtration is a solid-liquid separation process in which the liquid is forced through a porous medium and allows the deposition of solids on the filter medium. Depending on the desired application, the material of interest could be the solid, the liquid or both [1].

There are many means of increasing the filtration rate, such as increasing the filtration area and pressure drop across the filter cake, decreasing the viscosity of filtrate and thickness of the filter cake, or increasing the permeability of the cake. In this study, the effect of a filter aid on the permeability of the cake is taken into account in order to modify filtration and keep more solids in a deposition on the filter media [2].

Filter aids are used to mainly to adjust the solid phase of the material thus enhancing the filtration process. For hard-to-filter slurries, rapid medium blinding occurs, slowing down the filtration rate dramatically, and in extreme cases, stopping filtration all together. Filter aids can also improve the clarity of the filtrate and increase solids recovery. Filter aids are usually inert materials. The most commonly used filter aids include diatomaceous earth, expanded silica materials, and fibrous substances. There are also several other materials suitable as filter aids, such as Perilitic rocks, cellulose, non-activated carbon, ground chalks and ash. Organic substances such as wood fiber, sawdust and cellulose are finding increased uses as filter aids, due to their low cost and abundance [3].

Filter aids can be used as a pre-coat or a body feed (mixed with the slurry). As a pre-coat, the filter aid protects the filter media against the penetration of unwanted solids and premature blinding of the media. In practice, a combination of the two approaches is most common [4]. So if filter aids are added to the slurry, they are considered as body feed; and if they are placed as layer through which the solution part should pass they are called pre-coat [5].

Sawdust can be a good candidate as a filter aid and for treating the slurries, because its major constituents are cellulose, hemicellulose and lignin containing methyl esters that do not attach to metal ions. However, it should be mentioned that those constituents could be modified to carboxylate ligands by treating with a base such as sodium hydroxide, thereby increasing their metal-binding ability if desired to do so in any process [6].

Other advantage of using sawdust as a filter aid is that it can be incinerated and can provide better cake solidity. Calcined rice hull ash and fibers from used newspapers are relatively new filter aids. They are used for wastewater sludge dewatering [7, 8]. Sawdust fall as powder from wood as the wood is cut into lumber and it is considered as recyclable waste from the wood and timber industry. Since 1970s, saw blades have become thinner with more teeth, making the sawdust too small to be used as a fiber source for pulp. Different saw types generate sawdust of different size distributions; thus, some of them consist of particles that are too small to provide useful pulp [9].Therefore, sawdust is considered as a waste of wood processing industries that pollutes the environment but can become a valuable product if used properly in other industries such as energy, manufacturing, agriculture and environmental [10].

Some viscous suspensions like phosphoric acid sludge containing fine or colloidal particles are hard to make filter cake because of the fast pressure build up and medium blinding. However, addition of filter aids could assist in filter cake formation. Usually the proportion of the filter aid can be optimized based on the experiment [11].

Many slurries, including wet process phosphoric acid sludge, contain particles ranging from a few microns (μm) to mm size. Sometimes the fine particles can pass through the filter medium and report to the filtrate, which are called migrated particles [12].

In order to mitigate the effect of migrated particles in the acid and improve recovery of phosphoric acid, this study was designed to determine the effect of sawdust as a filter aid. Figure 1 shows the mechanism of filter aids in mitigating the migrated particles. In the case of phosphoric acid sludge, it is very important to mitigate the effect of migrated particles in the filtrate because these particles contain rare earth elements, the primary target of this research. These elements have significant applications in advanced technology, green energy generation,communication and defense industries [13].

Phosphate mining and processing streams phosphogypsum, phosphate clays, flotation tailings, and phosphoric acid sludge from the filter acid evaporation towers have low REE concentrations, but are available in very large volumes. This implies that these industrial processing streams could provide significant amounts of rare earths, if a practical and economic methodology is developed to recover them [14]. The REEs found in fine particles in the phosphoric acid sludge can pass through a filter media and migrate to the filtrate. Therefore, it is important to mitigate this phenomenon by adding appropriate filter aids to prevent them from migrating to the acid filtrate. This mechanism is shown in **Fig. 1**.

When filtering wet phosphoric acid sludge, filter cake forming on the surface of a filter becomes impermeable and prevents further filtration from occurring. Addition of a filter aid promotes a more permeable filter cake, which prevents deadlock. Filtering efficiency is improved by increasing the permeability of the filter cake via the use of filter aid because the filter aid assists in flow control and solid removal. Thus in this study, the effect of adding sawdust as a body feed to the phosphoric acid sludge was compared with saw dust as a pre-coat to the filter media.

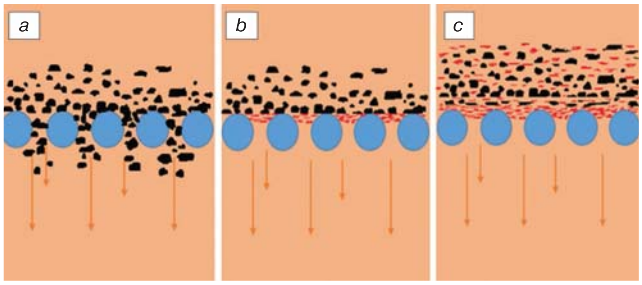

Fig. 1. Filtration without filter aids and how migrated particles ends in filtrate (*a*), filter aid as pre-coat on filter media (*b*), filter aids as body feed in slurry (*c*)

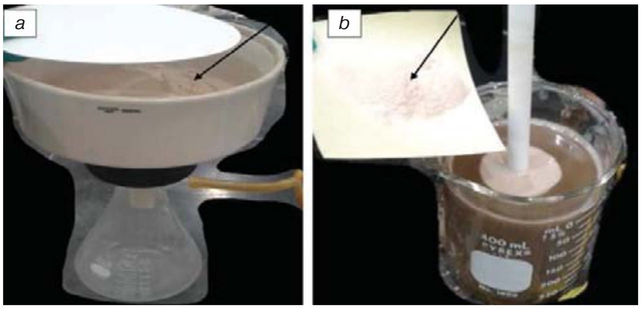

Fig. 2. Adding saw dust as pre-coat (*a*) andadding sawdust as body feed for filtration (*b*)

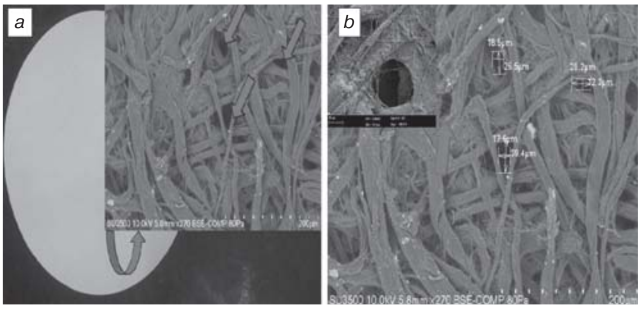

Fig. 3. SEM micrograph of the (*a*) filter paper (*b*) filter paper with cavity sizes

Methodology

Two sets of experiments were carried out to compare the pre-coat and body feed effect of sawdust on the filtration of phosphoric acid sludge. In the body feed experiment, 600 g of the as received phosphoric acid sludge was placed in a beaker and 100 g of gypsum-saturated water was added. To one of the samples, 3 g of sawdust (Maple leafy wood) was added. The sawdust flour was purchased from System Three Resins Inc., Auburn, WA with the average size of 88 to 177 μm. These samples were vacuum-filtered using a Buchner funnel with Whatman filter paper No. 40. The filter cake was washed two times and the amount of acid and deposited solid were weighted and recorded. The acid as a filtrate was filtered again to determine the amount of the migrated solids with the addition of two more filter papers stacked (No. 42 used in conjunction with No. 40). The same set of experiments was carried out for the pre-coat experiment. However, as it can be seen from **Fig. 2***a*, the 3 g of saw-dust was added as pre-coat within filter media and slurry was passed through the media for filtration and washing. In order to determine the effect of the sawdust dosage added as body feed, three dosage levels were tested at 0.5%, 1% and 1.5%, respectively. In all the experiments, filtration rate and REEs distribution were compared.

Results

Adding sawdust resulted in more solids in the final dry cake. **Table 1** shows the effect of sawdust by decreasing the migration of solids into the acid filtrated. The collected acid filtrate was filtered again and the amount of deposited migrated solid was recorded and shown in **Table 2**. About 0.83 g of solids were deposited on filter media for the sawdust treated slurry, but this value is 1.32 g for the slurry without sawdust, a 37% difference. For the

Table 1. Weights of the solid residue (Cake) and filtrate (Acid) in each set of experiment

Slurry Sample	Slurry weight, g	1st Acid, g	1st Wet Cake, g	Cake slurry, g	2nd Acid, g	2nd Wet Cake, g	Final Dried Cake, g
Body feed with 3 g Sawdust	603	353	247	374	152	222	132
No Sawdust	No filter aid was added (600 g)	376	224	324	140	184	124
Pre-Coat with Sawdust	600	351	249	141	150	199	141

experiment in which sawdust was used as a pre-coat, the amount of migrated solids was 0.57 g, showing improved performance in trapping migrated solid when sawdust was used as a pre-coat.

Figure 3 shows the SEM micrograph of the filter paper used in this study. The cavities and indention that the liquid particles can pass through is marked with red arrows. These tiny holes can be overlaid by the sawdust as filter aids trapping even tinier particles that contain the rare earth minerals. This phenomena and mechanism was explained earlier in Fig. 1.

Table 3 shows size distribution of the particles in the phosphoric acid sludge and **Fig. 4** shows a graphical particle size distribution curve. Phosphoric acid sludge was found to have a particle size range of 1.261 μm to 296 μm. These values can be compared with the filter cavity sizes shown in Fig. 3*b*. For example, on the filter paper, a cavity of 16.5 by 26.5 μm exists from which some smaller particles can migrate. However, this was mitigated by using sawdust as a filter aid.

Table 4 shows the Rare Earth distributions for the control test, pre-coat and body feed experiments both for final dried solids and collected acid. It is obvious that using saw dust as a filter aid, either in the form of pre-coat or body feed, has enhanced the filtration and fewer suspended solid particles have migrated to the filtrate (acid portion). The REE concentration in the final solids from the control test is 1659.79 ppm, but when saw- dust was used as a body feed and pre-coat, the REE concentrations in the solids were 2151.54 and 2098 ppm, respectively. With the exception of yttrium, concentration of all REEs in the solids fraction increased when sawdust was added. **Table 5** shows the amount of oxide substances and acidity of the solid residue and acid filtrate. As it can be seen, application of sawdust, either as a body feed or pre-coat, reduced P_2O_5 loss in the solids. This is important, not only for improving phosphoric acid recovery, but also for increasing leaching recovery of REE from the solids because phosphate causes precipitation of REE during acid leaching.

When the sawdust was used as a body feed, the permeability of the cake increased. The sawdust filter aid enhanced the filtration and, consequently, the clarification of the liquid acid filtrate. When the sawdust was added as a pre-coat, the quality of the filtrate phosphoric acid was even better due to less migrated solid particles. One assumption about the superior performance of the sawdust used as a pre-coat is that the pre-coat filter aid made the filter media less permeable to fine suspended solids. As the medium is the most important component of the filtration system, improving the filter media via pre-coating by sawdust prevented loss and migration of solid particles [15].

Table 2. Weight of the migrated solid particles in the filtrate (Acid)

Sample Re-filtered	Amount of solid trapped on filter media, g
1st Filtrate Acid (with dust experiment)	0.83
1st Filtrate Acid (without dust experiment)	1.32
1st Filtrate Acid (with dust as Pre-coat)	0.57

Table 3. Particle size statistics for phosphoric acid sludge

Data	Value	% tile	Size, μm
MV(μm): mean volume average diameter	46.63	10	2.913
MN(μm): mean number average diameter	2.210	20	5.070
MA(μm): mean area average diameter	9.75	30	14.81
CS: Calculated surface area	0.615	40	27.24
SD: standard deviation	39.71	50	38.08
Mz: Graphic Mean	41.78	60	48.36
σι: Inclusive Graphic Standard Deviation	39.59	70	59.84
Ski: Inclusive Graphic Skewness	0.2946	80	74.93
Kg: Kurtosis Peakedness	0.914	90 95	102.0 132.4

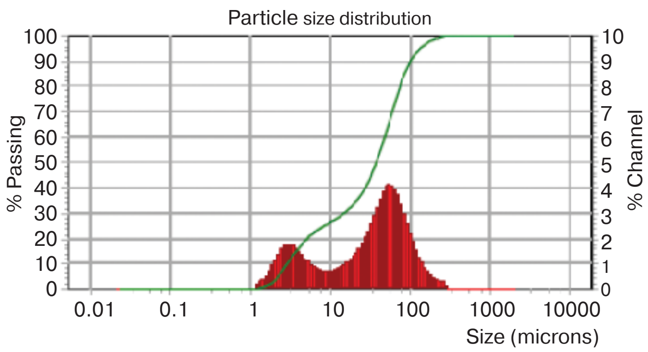

Fig. 4. Particle size distribution curve for phosphoric acid sludge

Table 4. ICP results of the Rare Earth Elements (ppm) in solid residue and filtrate

Rare Earths	Control Test Solid	Body feed Dust Test Solid	Pre-coat Dust Solid	Control Test Acid	Body feed Dust Test Acid	Pre-coat Dust Acid
Sc 45	10.15	7.84	6.4	1.7	1.3	1.7
Y 89	422.69	334.85	371.4	25.02	22.71	25.6
La 139	292.26	430.59	419.0	3.68	6.38	6.3
Ce 140	381.29	602.12	574.9	4.73	8.08	8.1
Pr 141	50.26	79.89	78.7	0.64	1.09	1.1
Nd 142	196.96	333.45	300.5	2.6	4.57	4.3
Sm 152	57.03	83.97	76.4	0.78	1.4	1.3
Eu 153	15.38	21.05	19.9	0.23	0.38	0.4
Gd 158	95.35	120.68	115.5	1.43	2.3	2.2
Tb 159	12.97	14.78	14.2	0.23	0.31	0.3
Dy 164	74.42	77.55	76.0	1.69	1.96	2.0
Ho 165	13.50	12.84	13.3	0.44	0.44	0.5
Er 166	28.27	25.25	25.0	1.78	1.59	1.7
Tm 169	2.02	1.53	1.6	0.36	0.29	0.3
Yb 174	6.38	4.55	4.6	2.85	2.15	2.5
Lu 175	0.86	0.60	0.6	0.59	0.43	0.5
Total REE	1659.79	2151.54	2098	48.75	55.38	58.8

Table 5. ICP results for oxides found in the solid residue and filtrate

Substance	Control Test Solid	Body feed sawdust Test Solid	Pre-coat Sawdust Solid	Control Test Acid	Body feed Dust Test Acid	Pre-coat Dust Acid
% P_2O_5	22.22	15.53	13.98	23.19	18.91	17.86
% MgO	2.24	3.60	5.7	0.50	0.27	0.29
% Al_2O_3	3.23	4.76	7.81	0.47	0.36	0.37
% Fe_2O_3	4.74	2.99	4.83	0.45	0.39	0.40
% CaO	12.26	11.30	12.36	0.81	0.96	0.23

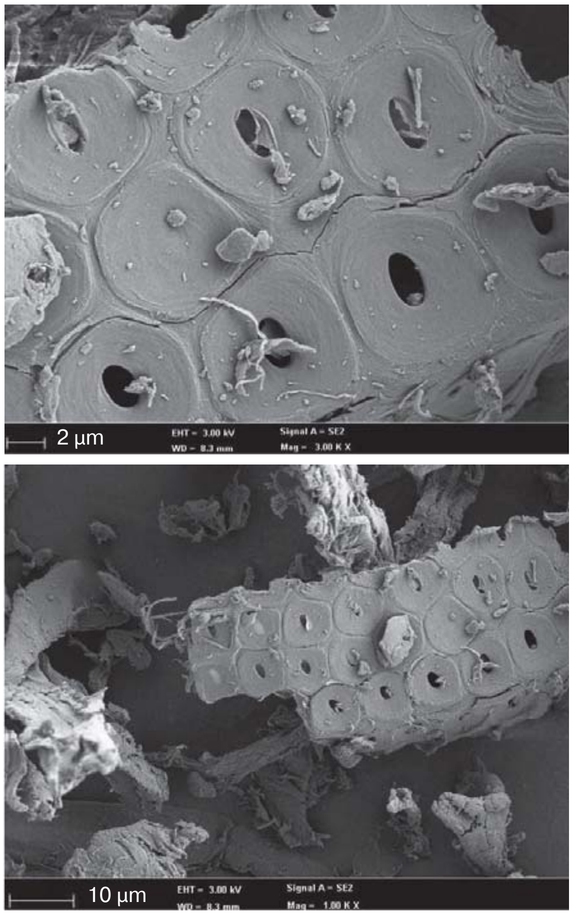

Fig. 5. SEM micrographs of sawdust

Cake compressibility is decreased when filter aid is added as body feed due to the "admix "effect. The filter aids form a thin and rigid layer with high porosity and have a narrow fractional size distribution for removing the finer fraction. Saw dust filter aid is chemically inert thus preventing medium clogging [16]. The surface SEM micrographs of sawdust is shown in **Fig. 5**. The porosity of the sawdust enhances trapping finer solid particles and prevents them from migration to the acid filtrate [17].

Table 6 shows the results for the different dosages of saw-dust as body feed As it can be seen , when the dosage of the saw dust was increased from 1% to 1.5% less rare earth have been distributed in the final solid residue as well as liquid acid filterate. So it can be concluded that when dosage is increased, it will affect the slurry treatment for REE distribution aversely. **Figure 6** shows that addition of sawdust enhanced the rate of filtration (Saw dust is taken into account for calculation of Solid %). However, comparing 1% with 1.5% of sawdust aaddition, 1% sawdust produced the best results in terms of rare earth distribution in final solid. In terms of solid percent in the filter cake, pre-coat proved to be more effective generating a cake. Thus, it can be said that addition of optimized amount of saw dust as pre-coat and body feed was effective in retaining more rare earth elements in slurry cake; with conclusion of 0.5% saw dust addition in body feed form providing the best result. This cake could later be utilized and processed further for recovery and stripping of rare earth elements from acid as well as solid cake by reported hydrometallurgical methods such as crystalization, precipitation, ion exchange, solvent extraction and specifically leaching of the solid part with H_2SO_4, HNO_3, HCl acids in which saw dust is dissolved to its components [18].

Conclusion

The effect of using sawdust as a filter aid was investigated for filtration of phosphoric acid sludge, in order to recover REEs and phosphate. Utilization of sawdust, both in the form of body feed and pre-coat, showed improvement of filtration rate and REE recovery. The performance of pre-coat versus body feed sawdust application mode was compared. It was found that using sawdust as body feed in the filter media enhanced the

Table 6. REE distribution in the final solid and liquid portion for the 1% and 1.5% of saw dust dosage

Element	1% saw solid	1.5% saw solid	Acid 1% saw	Acid 1.5% saw
Sc 45	5.52	4.85	1.48	1.18
Y 89	294.53	254.12	27.86	23.09
La 139	309.4	262.48	6.68	5.61
Ce 140	425.65	360.35	8.65	7.31
Pr 141	58.27	47.73	1.16	0.98
Nd 142	225.99	187.92	4.73	3.99
Sm 152	57.02	47.13	1.38	1.15
Eu 153	14.89	12.28	0.39	0.33
Gd 158	84.75	70.09	2.32	1.96
Tb 159	10.49	8.65	0.32	0.27
Dy 164	55.56	46.04	2.06	1.72
Ho 165	9.75	8.12	0.49	0.41
Er 166	18.51	15.35	1.72	1.4
Tm 169	1.18	1	0.32	0.26
Yb 174	3.54	3.07	2.43	1.96
Lu 175	0.47	0.41	0.48	0.39
Total REE	1575.51	1329.59	62.47	50.05

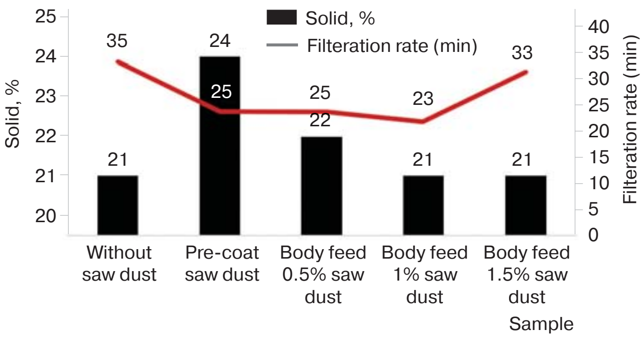

Fig. 6. Solid % and filteration rate for all the treated samples

filtration by collecting more distribution of Rare Earth Elements in the solids. Addition of sawdust in pre-coat form was most effective for preventing rare earths migration into the acid part.

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