Agglomeration-flotation: a laboratory technique for prediction of bitumen recovery from oil sands fine tailings

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Agglomeration-Flotation: A Laboratory Technique for Prediction of Bitumen Recovery from Oil Sands Fine Tailings

by

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Abstract

Suncor Oil sands mature fine tailings contain about 30 percent by weight of solids and 3 percent by weight of bitumen. Of the total solids, ultrafines (<0.5 μm) represent about 12 wt%. These materials can be separated from the fine tails and may be used as value added products. The removal of bitumen from fine tails is the first part of a two part investigation into the separation of value added materials from oil sands fine tailings for use in a variety of applications.

Laboratory techniques, previously developed to determine the potential for beneficiation and recovery of oil agglomerated waste fine coal, have given results in good agreement with results from pilot or full scale operations. Similar techniques have been used to evaluate the recovery of residual bitumen from a sample of Suncor fine tails using a typical power station ground coal as the absorbent.

At room temperature, the coal was preconditioned with No. 2 fuel oil, subjected to a 30 second high shear mixing step and then collected by flotation during a 3 minute period. Float recovered coal was contacted with mature fine tailings (MFT) for 5 minutes, using low shear mixing conditions. A 5 minute flotation resulted in the recovery of 93 percent of the residual bitumen. Equipment required for the process has already been designed, scaled and operated in fine coal recovery.

INTRODUCTION

The treatment of oil sands mature fine tailings (MFT), for lease restoration, represents an economic burden to the existing surface mining plants in the Athabasca area of Alberta. Oil sands fine tailings is a complex mixture of several components, each having specific physical or chemical characteristics. Results have been reported on the separation of fine tailings into a number of components[1]; these materials are believed to have commercially useful properties. Studies on the fundamental properties of fine tailings have resulted in the development of methods to separate these components into relatively "pure" fractions[2]. An initial assessment of the properties of these materials for commercial applications has identified the potential tailings products shown in Table 1.

Bitumen represents a significant component of fine tailings and its presence also causes some difficulties in the separation of other useful fractions in a form suitable for commercial use. Consequently, the efficient separation of bitumen from fine tailings represents a prerequisite first step to any subsequent treatment for component fractionation. Liquid phase agglomeration techniques have been previously applied to oil sands fine tailings for bitumen separation[3]. In this earlier work the need for tailings dilution and long mixing times made the process unsuitable for commercial application.

Component	Application	C (%)	Size (μm)
Bitumen	SCO[1] production or ancillary fuel after pelleting with limestone		
Kaolin	Fine paper coating	<1	0.3-0.5
Emulsifying Solids	Substitute for surfactants in emulsification e.g. of asphalt	12	<0.3
Gelling Agent	Replacement for swelling clay in drilling mud and propping compounds		<0.3
Heavy Metals	Source of rutile and vanadium		
- CBS[2]		12	<44
- HPS[3]		30-50	<44

Table 1: Fine Tailings Components with Potential Commercial Applications.

[1] SCO is synthetic crude oil; [2] CBS is coarse biwetted solids;
[3] HPS is hydrophobic solids.

The National Research Council has extensive experience with oil agglomeration for the recovery of fine coal. Work has encompassed process demonstration at the laboratory, pilot and commercial scale. Carbon recoveries of over 90% can be achieved by using a processing sequence of 0.5 min high shear mixing, 3 min low shear mixing and 5 min of flotation to produce coal-oil froth[4]. Results from laboratory tests have been verified at both the pilot and commercial plant scale[5-6]. This work has demonstrated the feasibility of predicting full scale process behaviour from small scale trials.

Heavy metals, present in oil sands, tend to be associated with concentrations of strongly adsorbed organic matter in relatively large aggregates[7]. As a result, this fraction tends to have hydrophobic surface characteristics and is usually closely associated with bitumen. Consequently, during a flotation process, heavy metals are more likely to report with the froth. The current investigation was conducted to determine whether or not existing agglomeration-flotation experience with coal could be applied to the removal of bitumen and heavy metals from fine tailings. In this approach the fine tailings are subjected to a low shear mixing with pre conditioned ground coal or coke followed by separation of the resulting amalgam using conventional flotation.

Experimental

Bitumen Separation

In previous work, ground but otherwise untreated, refinery coke, from either Syncrude or Suncor, was used to collect the bitumen from MFT material[3]. Satisfactory recoveries were only achieved by diluting the tailings and mixing at high speed for up to 40 min. In the current tests on Suncor MFT, these shortcomings were successfully overcome by pretreating the bitumen collector phase (coal or coke) with a small amount of light fuel oil to improve its bitumen adsorbtivity. In this way the efficiency of bitumen capture was improved and the need for tailings dilution and long mixing times was eliminated. A simulated continuous process was conducted by performing multi-batch runs.

In Stage 1 coal (75g), supplied by the Cape Breton Development Corporation (CBDC), was first thoroughly wetted by adding it to pond water (500mL) in a 1L Waring Blendor jar and mixing for about 2 min, using low shear agitation. Preconditioning was accomplished by adding #2 fuel oil (2% based on dry coal) to the Blendor jar and mixing the contents, under high shear conditions, for 30 sec. The contents of three Blendor jars were transferred to the stainless steel cell (1.5L capacity) of a Denver Laboratory Flotation Machine, Model # D-12. The flotation machine was operated at 1100 rpm with air aspirated at a rate sufficient to maintain a persistent foam. Froth was skimmed from the flotation cell surface for 3 min or less and was collected on a 325 Tyler mesh screen. Any fine tailings passing through the sieve were combined with the flotation cell residue. Froth and tailings fractions were collected and weighed. The froth fraction contained the bulk of the oil conditioned coal to be used for bitumen collection.

For Stage 2 a sample of Suncor MFT (500mL) was placed in a 1L Blendor jar and 15 w/w% (d.b.) of conditioned coal froth added along with about 0.016 kg/t of frother. The resulting slurry was mixed for 5 min under low shear conditions. Again, the procedure was repeated three times to provide enough feed for a flotation test. Flotation of the combined feeds was carried out as previously described and the froth and tailings collected.

Stage 3 is an optional froth washing step. Rougher flotation cell product (50g dry solids), from Stage 2, was diluted with pond water (500mL) in a Blendor jar to give a suspension containing about 10 w/w% solids. The contents of the jar were washed by mixing for 2 min under low shear conditions. Three samples of washed rougher concentrate (1.5L) were combined in the Denver Flotation Machine cell, which was then operated under the conditions described earlier. Froth was skimmed from the flotation cell surface for 3 min, collected and weighed. A simple schematic representation of the three stages of bitumen separation is shown on Figure 1.

Bitumen, water and solids contents were determined on representative samples from all streams, using a modification of Syncrude Analytical Method 2.8[8]. These results are summarised in Tables 2 and 3; an important determination was that over 95% of the bitumen could be recovered from undiluted fine tailings while using short mixing and flotation times. This represents a major advance over previous experience[3].

Tailings Analysis

An important aspect of this work was to determine the distribution of tailings components. Each of the various streams from the bitumen agglomeration-flotation test on Suncor MFT was examined. Three samples were analysed directly, namely: fine tailings feed, primary tailings and secondary tailings. The type and composition of MFT solids in the coal-bitumen froth products were evaluated indirectly, based on the individual component analyses summarised in Table 3. A determination of total organic carbon (TOC) on the tailings water, before and after bitumen separation, showed a reduction of about 25% to 150ppm.

Feed, rougher tailings and cleaner tailings were analysed to determine total solids, total ultra fines fraction (<0.5mm) and biwetted ultra fines (BUS) using the method decribed by Kotlyar et al[2]. Each determination was carried out in duplicate.

Discussion

Flotation Test

Consideration of Table 4 shows that bitumen recovery in the rougher flotation step was 95.7%, while overall recovery, after froth cleaning, was 93.4%. These numbers compare very favourably to previous test work where recoveries of only 85% of bitumen were obtained[3]. In the latter case the product was in the form of coke-bitumen agglomerates (1-2mm in diameter) rather than a froth, as in the present work. Even though coal, rather than coke, was used as the bitumen collector in the present flotation-agglomeration work this result indicates that preconditioning with oil promotes collector-bitumen contact and adhesion, thereby allowing much shorter collection times to be used. For example, a flotation time of only 5 min was needed compared to at least 20 min for agglomeration. The process conditions identified for high bitumen recovery appear to be compatible with a technically and economically feasible tailings treatment process.

The cleaned froth contained 17.8% bitumen, 28.9% solids (22.2% coal) and 53.3% water. Previous experience with this type of material indicates that further dewatering should be possible by use of conventional agglomeration equipment; water reduction to about 20% is typical. Even so, this bitumen concentrate may not be acceptable for conventional froth treatment. In this case the material may be blended with ground limestone to produce composite fuel pellets, having excellent combustion and sulphur retention characteristics[9].

From the froth analysis data, Table 3, it is possible to estimate the amount and type of MFT solids in the various flotation streams; in this respect carbon content is a good indicator for solids classification. The product from the initial Stage 2 rougher flotation contains 55.8% MFT solids. This represent 25.6% of the total MFT solids at a carbon content of 13.7%. Following stage 3 cleaning the froth solids content was reduced to 23.2% MFT solids representing 6.0% of total MFT solids, with a carbon content of 37.8%. The latter calculated carbon content is typical for hydrophobic solids (HPS) separated from fine tailings in other work[10]. This is not an unexpected result as this hydrophobic material is defined by its strong interaction with bitumen.

One can conclude that the bulk of the hydrophobic solids and associated heavy metals have reported with the flotation froth. Table 4 shows that copper, titanium and zirconium are preferentially retained in the product streams. Nickel, chromium and vanadium are split proportionally between product and tails. If the froth product is used as a fuel, then the ash from combustion would represent a highly concentrated metal source for extraction. It is known that the presence of calcium has a beneficial effect on the acid leaching of vanadium and nickel from coke ash[11]. Hence, coagglomeration of the bituminous froth with limestone will have the added advantage that the ash from the burnt fuel will be eminently suitable for heavy metal recovery as a by-product of the combustion process.

A similar analysis of the tailings streams has been made. The solids in the rougher tails have a carbon content of 7.8%. This is typical for mixtures of both coarse and fine hydrophilic and biwetted solids. The tailings solids from the Stage 3 froth cleaning step had an estimated carbon content of 13.8%, which is similar to values reported for biwetted solids[10]. The results indicate that although these solids were hydrophobic enough to be floated in the initial separation step they were not sufficiently strongly bound in the froth to be retained during the washing stage. Consequently, the cleaner tails may represent a concentration of both coarse and fine biwetted solids in an amount representing about 6.0% of MFT.

Consideration of Table 4 allows a better appreciation of the distribution of useful components among the different streams. From the previous interpretation of data the dramatic drop in solids content of the rougher tails is believed to be almost entirely associated with the separation of hydrophobic and coarse biwetted solids with the bituminous froth.

The corollary to this observation is the increase in the total ultra fines concentration in these tails and a relative decrease in biwetted solids. Complete separation of the cleaner tails could not be attempted but the results show a corresponding increase in biwetted material concentration relative to the rougher tails.

In summary, it has been determined that almost quantitative recovery of bitumen from MFT can be achieved. The solids fractions containing the bulk of the heavy metals are also concentrated with the bitumen but the less hydrophobic material is released into the cleaner tails when the bituminous froth is washed; the solids in these secondary tailings are richer in both coarse and ultra fine biwetted material. The flotation process results in the ultra fine solids being concentrated in the rougher tails and this fraction therefore provides a "clean" source of this component. As a result of this favourable distribution of tailings components any additional fractionation to produce the specified commercial products will be a relatively simple matter.

Figure 2 shows the flow diagram for a conceptual pilot plant to treat 5 tph of fine tailings solids for bitumen recovery. The design is based on previous demonstration and commercial experience for recovery of fine coal from wash plant waste and tailings ponds. Modification have been made for fine tailings treatment.

In stage 1, raw coal (1) is ground (70% - 200 mesh) and mixed with pond water (2) to produce a slurry of about 15% solids. Residence time is about 3 minutes. The coal slurry stream (3) and an agglomerating oil (4) (e.g. No. 2 fuel oil at 2%, based on dry coal) are fed to a high shear mixer and mixed for 30 sec to agglomerate the coal. The slurry of agglomerated coal (5) then passes to a flotation cell where the coal flocs are concentrated as a float material (6); the tailings (7) contain some solids and are sent to a thickener for water recovery. Residence time in the float cell is about 3 min.

For stage 2, coal float material (6) from stage 1 is mixed with mature fine tails (8) and frother (9) in a turbine agitated, low shear mixing vessel for 5 min before transfer, as stream 10, to a second flotation cell. Residence times of about 3 minutes are required in this vessel. Coal-bitumen float material and tailings leave the cell as streams (11) and (12) respectively. Tailings stream (12) provides the feed for any subsequent treatment to recover other tailings products. For a commercial operation the solids content of this stream has been calculated to be about 30% compared to 17.5% for the batch process.

Stage 3, is an optional step to improve the quality of the rougher flotation product. The coal-bitumen float material (11) passes to a turbine agitated, low shear mixing vessel where it is diluted with pond water (13) to give a solid content of about 10%; a mixing time of about 2 min is used at this stage. Final separation of the coal-bitumen float material occurs in third flotation cell to give a cleaned product stream (15) and a dilute tailing (16), containing insufficient solids to justify further treatment. The tailings are sent to a thickener for water recovery.

Figure 3 shows a conceptual separation scheme used to obtain various value added products[2]. Bitumen and heavy metal components are first removed. Other useful fractions may then be separated, using a series of centrifugation steps, to fractionate the solids by particle size, for specific applications. Primary tailings from the coal-bitumen separation are centrifuged at 200 X G to remove coarse (>0.5 μm) solids, which consist mainly of silica. The remaining suspension contains the total ultrafines (≤0.5 μm). This suspension is further separated by centrifuging at 1500 X G to remove the coarse ultrafines (0.3-0.5 μm), which consist mainly of kaolin. The latter can be used as a coating material in fine paper production. The remaining suspension contains biwetted ultrafines, which are used as emulsifying solids, and hydrophilic ultrafines, which are used as gelling agents. These components are separated by emulsion flotation.

About 30% of the mature fine tailings solids are recoverable as useful products. The remaining solids are relatively coarse and settle readily to a dense sediment for easy disposal.

Further work will be required to determine the magnitude of the Alberta market for the envisaged tailings products. Also, product specification requirements must be more closely defined and the possibilities for product substitution confirmed. The separation process economics should then be evaluated in more detail.

Conclusions

Preliminary testing has demonstrated that the use of oil conditioned coal, in an agglomeration-flotation process, allows almost quantitative recovery of bitumen from oil sands fine tailings. This is an essential first step prior to subsequent separation of the other value added components. The basic process steps and conditions for tailings treatment have been identified but not completely defined. Further work will be required to determine market size and product specification. Tests should be performed to confirm the possibility for product substitution.

Acknowledgements

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Table 2: Product Qualities and Recoveries of Feed Materials and Separated Fractions

	Feed and Product Qualities					Unit Operations Recoveries		
Fractions	Bitumen (%)	Solids (%)	Water (%)	Ash* (%) (m.o.f.)	Carbon (%) (m.o.f.)	Bitumen (%)	Yield (%) (m.o.f.)	Carbon (%) (m.o.f.)
Feed Materials								
Coal	----	100.0	----	8.3	91.7			
MFT	5.0	28.2	66.8	89.5	10.5			
Pond Water	----	0.23	99.8	89.5	10.5			
STAGE 1 (CoalConditioning)								
Product	----	30.0	70.0	6.2	93.8	----	95.4	97.6
Tailings	----	2.0	98.0	52.2	47.8	----	4.6	2.4
STAGE 2 (Rougher Flotation)								
Product	9.1	25.2	65.7	50.9	49.1	95.7	38.2	79.5
Tailings	0.18	17.5	82.3	92.2	7.8	4.3	61.8	20.5
STAGE 3 (Cleaner Flotation)								
Product	17.8	28.9	53.3	19.2	80.8	97.6	56.4	88.4
Tailings	0.02	1.2	98.8	86.2	13.8	2.4	43.6	11.6

Note: m.o.f. is moisture and organic free basis. *Ash content is of solids component only.

Table 3: Fine Tailings Contribution to Flotation Products

	Product Qualities					Recoveries	
Fractions	Bitumen (%)	Solids (%)	Water (%)	Ash* (%) (m.o.f.)	Carbon (%) (m.o.f.)	Yield (%) (m.o.f.)	Carbon (%) (m.o.f.)
STAGE 1							
Product	-	30.0	70.0	6.2	93.8	95.4	97.6
Tailings	-	2.0	98.0	52.2	47.8	4.6	2.4
STAGE 2							
Product	9.1	25.2	65.7	50.9	49.1	38.2	79.5
Estimated Coal	-	-	-	6.2	93.8	95.4	97.6
MFT Solids	-	-	-	-	13.7	25.6	-
Tailings	0.2	17.5	82.3	92.2	7.8	61.8	20.5
STAGE 3							
Product	17.8	28.9	53.3	19.2	80.8	56.4	88.3
Estimated Coal	-	-	-	6.2	93.8	98.0	98.0
MFT Solids	-	-	-		37.8	6.0	-
Tailings	0.02	1.2	98.8	86.2	13.8	43.6	11.7

Note: m.o.f. is moisture and organic free basis. *Ash content is of solids component only.

Table 4: Distribution of Heavy Metals in Flotation Product and Tailings Fractions

Fraction	Heavy Metal Concentration (m.f.) ($X10^{-4}$)						Mass Yield (m.f.) (%)	Heavy Metal Recovery					
	NI (%)	Cr (%)	V (%)	Cu (%)	Ti (%)	Zr (%)		NI (%)	Cr (%)	V (%)	Cu (%)	Ti (%)	Zr (%)
Coal Feed	9.90	9.13	20.75	1162.0	415	10.79							
MFT Feed	76.02	76.02	319.30	15.97	7374	190.10							
Product 1	104.7	59.84	205.70	314.20	7854	231.90	45.44	52.91	41.47	47.19	75.70	67.81	69.01
Tails 1	77.60	70.30	191.70	83.99	3104	86.73	54.56	47.09	58.53	52.81	24.30	32.19	30.99
Product 2	130.80	44.03	166.60	464.10	8092	214.20	67.26	67.87	51.61	66.87	73.75	80.66	81.22
Tails 2	127.2	84.80	169.60	339.20	3985	101.80	32.74	32.13	48.39	33.13	26.25	19.34	18.78
Product 2 Ash	1100	370	1400	3900	68000	1800							

Table 5: Distribution of Solids Fractions Between Streams from Bitumen Flotation Step

Sample	Total Solids Content (w/w % of MFT)	Total Ultra Fines (% of Total Solids)	Biwetted Ultra Fines (% of Total Ultra Fines)	Biwetted Ultra Fines (% of Total Solids)
MFT Feed	32.2 ± 0.5	17.3 ± 0.7	9.8 ± 0.1	1.0
Rougher Tails	17.9 ± 0.7	23.2 ± 1.8	5.7 ± 1.2	0.6
Cleaner Tails	1.2 ± 0.1	80.0 ± 1.2	9.9 ± 0.2*	ND

Note: All results calculated on bitumen free dry solids basis
* Determination measured combined fine and coarse biwetted solids

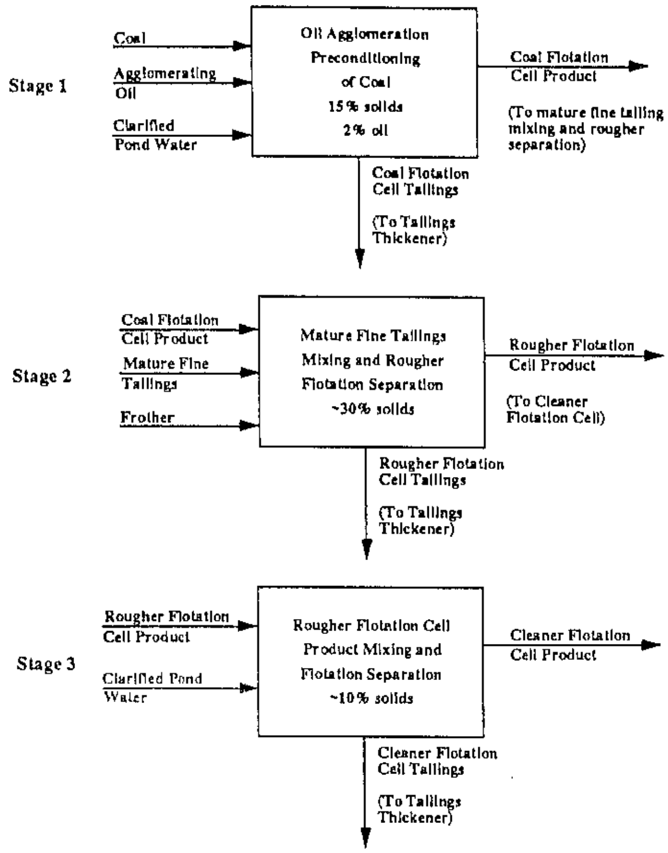

Figure 1: Simple Schematic of Three Stage Bitumen Separation Procedure

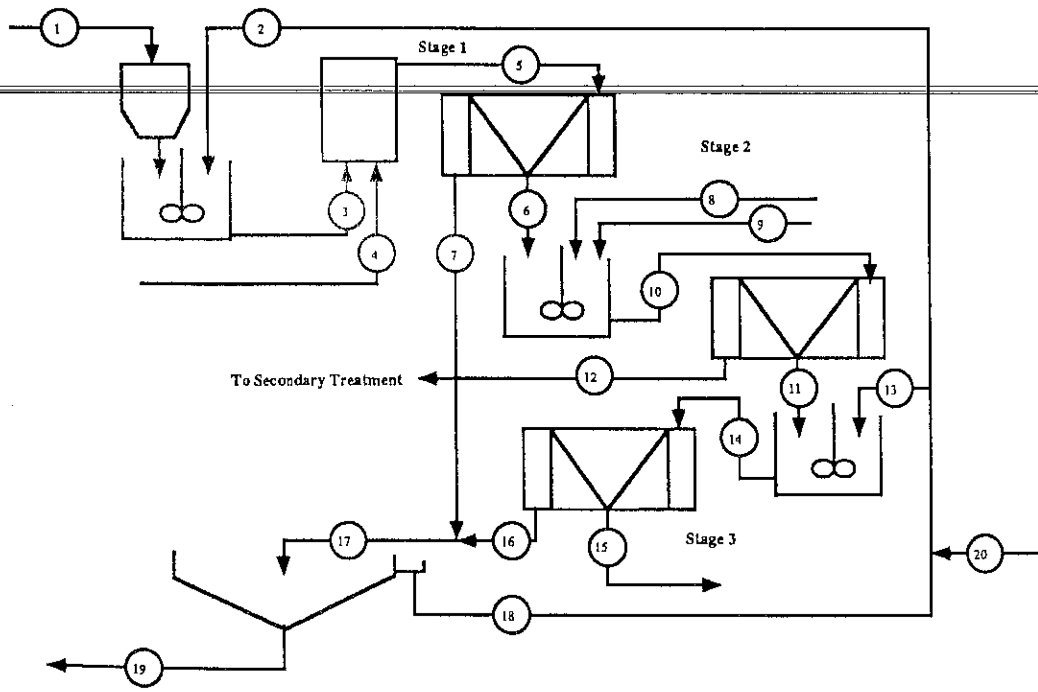

Figure 2: Conceptual Pilot Plant To Treat 5 Tph Of Solids From Fine Tailings

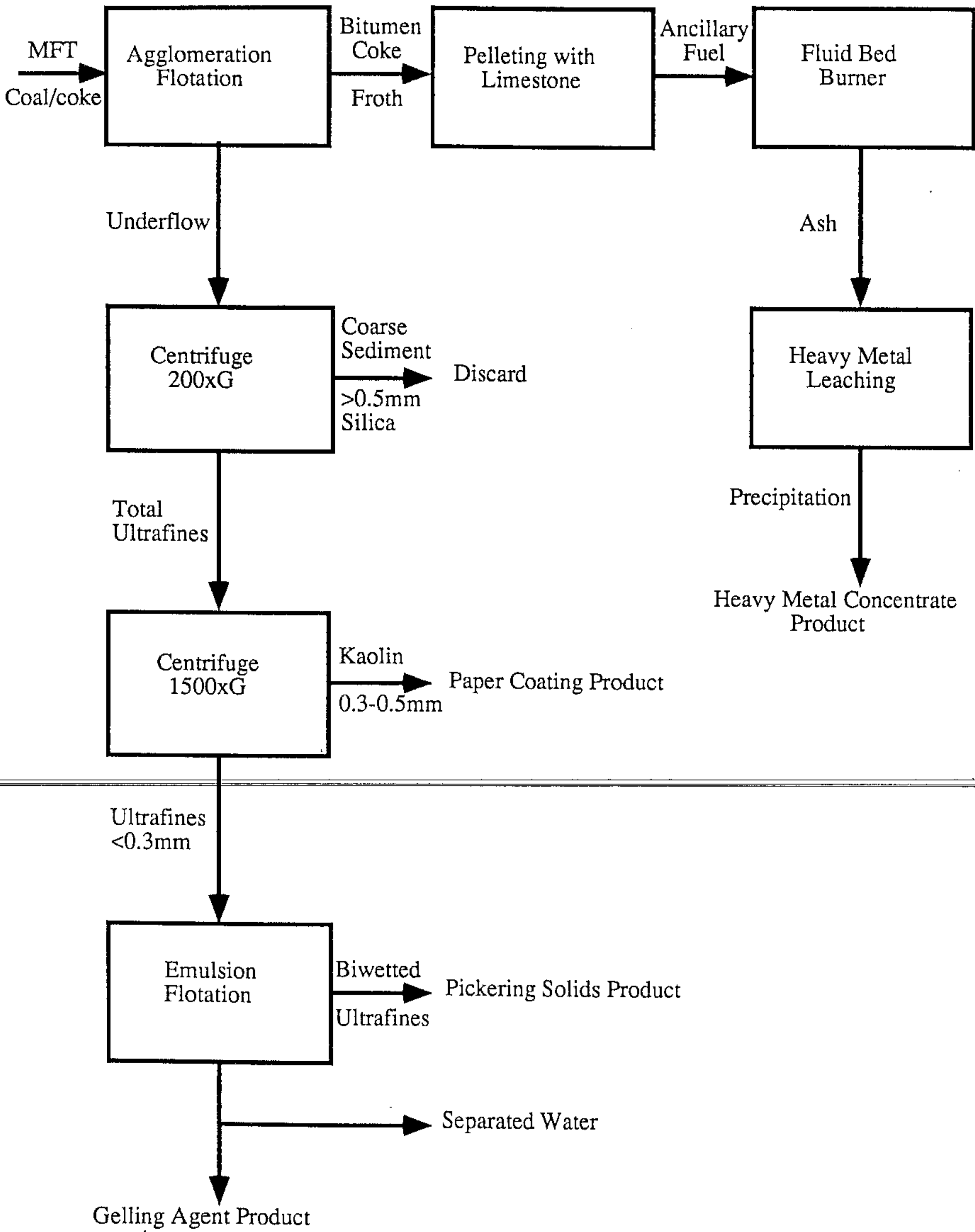

Figure 3: Overall Conceptual Block Flow Diagram for Product Separation from MFT

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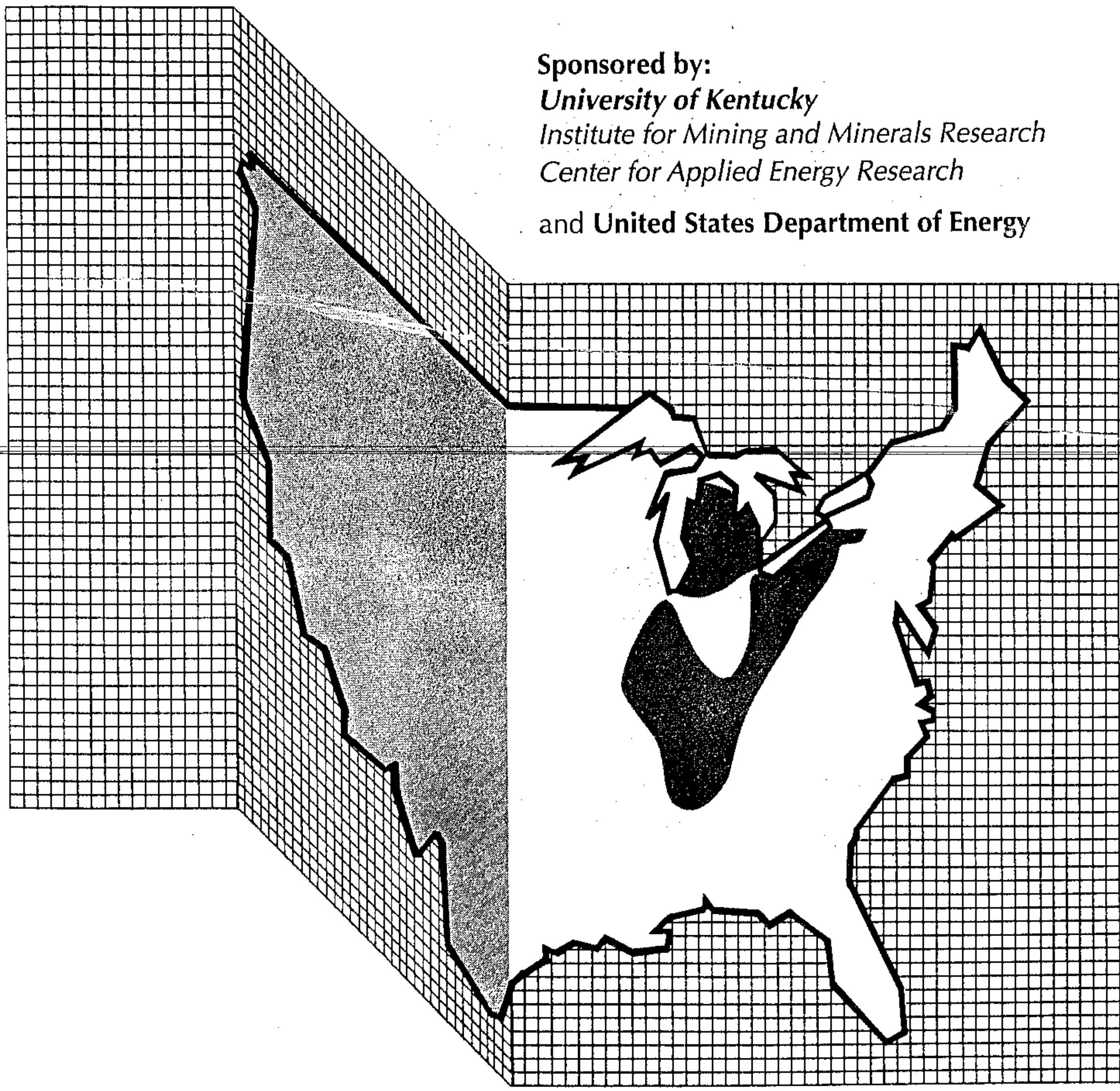

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