RESEARCH NOTE

EFFECT OF SURFACTANT ON SPHERICAL OIL AGGLOMERATION OF COAL

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(Received: December 7, 1999 - Accepted in Final Form: June 12, 2001)

Abstract In this paper, the results of the Spherical Oil Agglomeration of .45 micrometer super pits low grade coal particles (Bagworth Colliery, U.K.) within a suspension are presented. Demineralized agglomerates were recovered directly by sieving on a 106 micrometer sieve. Very good reductions in the ash content of the feed coal samples were achieved. In order to reduce the high levels of the crude oil dosage comparatively, small quantities of surfactants were added to the suspension. Of the various surfactants screened, Triton x.405 (non.ionic) proved to be very efficient and a crude oil reduction of over 60 wt% was achieved for concentrates containing 8 wt% ash.

Key Words Spherical Oil Agglomeration, Surfactant, Coal, Crude Oil

چکیده اگلومراسیون کروی نفتی ذرات زغال سنگ کم عیار با اندازه‌های زیر ۴۵ میکرون از معدن زغال سنگ بگورث انگلستان بررسی شد. اگلومریتهای حاصله مستقیماً روی سرندی به دهانهٔ ۱۰۶ میکرون بازیافت شد. تجزیهٔ اگلومریتها نشانگر کاهش قابل ملاحظه در محتوای خاکستر خوراک اولیه بود؛ ولی به علت مصرف زیاد نفت سیاه، این روش از نظر اقتصادی مناسب بنظر نرسید. لذا به منظور کاهش مقدار نفت سیاه مصرفی، مقدار کمی ترساز به سوسپانسیون اضافه شد. از میان ترسازهایی که آزمایش شدند، تریتون X-405 (غیر یونی) کارایی بالایی داشت؛ بطوریکه با ۶۰٪ وزنی کاهش در مصرف نفت، مقدار خاکستر نهایی محصول ۸٪ وزنی گزارش شد.

INTRODUCTION

Fine particles in liquid suspension can be agglomerated in a number of ways. One of the oldest procedures involves the addition of electrolytes to the suspension to cause a reduction in the zeta potential which allows colliding particles to cohere [1]. A second method involves the use of polymeric flocculents which bridge between particles. A third method, Spherical Oil Agglomeration (SOA), "Puddington Process", involves the addition of a second immiscible liquid, which preferentially wets the hydrophobic particles resulting in adhesion by capillary interfacial forces. While the bonding forces in the first two methods are small and result in rather weak and voluminous agglomerates, the Spherical Oil Agglomeration method produce more dense and much stronger agglomerates, which can be separated by sieving. In the case of fine coals, the carbonaceous constituents can be agglomerated and recovered from the aqueous suspension with many different oils as collecting liquids. Inorganic or ash-forming constituents remain in suspension and are rejected. Like froth flotation oil agglomeration relies on differences in the surface properties of coal and minerals to effect a separation. Froth flotation, however, becomes less effective where extremely fine (-63 micrometer) particles of coal must be treated, whereas there is no lower limit on the particle size suitable for agglomeration.

Agglomeration with the help of oil has been used by Puddington et al [2,3] for graphite, chalk, zinc, sulfide, coal, iron ore,and tin ore in aqueous solution. Abdulrahman et al [5] studied the effect of surfactant on oil agglomeration of fine coal. They were able to reduce the oil consumption by up to 20% by weight with various surfactants.

Samples Preparation The coals and the shales were obtained from the Bagworth Colliery in South Leicestershire Coal Field, UK (a summary of the various fractions is presented in Table 1). The samples, using a laboratory cone crusher, were crushed to less than 5 mm in diameter then milled in a Kek Mill three times, before feeding them into a Locker "Rotex" triple deck screen by means of a vibrating hopper.

The process of milling and screening was repeated until enough -45 micrometer samples were collected, put into resealable polythene bags and kept in dark and dry place in order to minimize any possible oxidation.

EXPERIMENTALMETHODS AND PROCEDURES

Agglomerates Formation In preliminary spherical oil agglomeration experiments, in order to find an economically suitable agglomerating reagent, a 10% by weight (50 g

TABLE 1. Ash Content (%wt) of Various Coal and Shale Samples.

Samples Source	Ash Content(%wt)			
	Size (micrometer)			
	-45	45-104	104-250	+250
Bagworth Coal	49.0	32.0	19.13	17.3
Bagworth Coal (Rank 902)	16.91	14.24	10.24	8.07
Bagworth Shale	85.59	77.51	72.80	68.67
Shirebrook Coal (Rank 702)	10.0	9.0	9.0	8.7
Shirebrook Shale	82.0	75.74	68.12	63.32
Bagworth R.O.M.	21.0	15.0	13.0	10.5

TABLE 2. Screening Results for Choosing a Suitable Agglomerating Reagent.

Experimental Conditions:
- Coal and Shale Origin = Bagworth Colliery
- Solids Concentration = 10% wt
- Suspension pH = Natural (6.90)
- Reagents Dosage = 10gr/50gr Feed Coal
- Agitator Speed = 3500 rpm
- Agglomeration Time = 4 minutes
- Feed Coal Ash Content = 51.25% wt
- Weight of Feed Coal = 50 gr
- Weight of dmmf Coal in Feed = 24.38 gr
- Weight of Ash in Feed = 25.62 gr

Reagents	Cost,1989(Pound/10gr)	Aggl.Ash(% wt)
Toluene	0.046	9.5
Xylene	0.063	6.13
Cooking Oil	0.0068	6.50
Crude Oil	0.00052	8.15
Diesel Oil	0.0043	9.18

sample in 500 cubic centimeter distilled water) solids concentration of artificial coal-shale mixtures (50/50 w/w) were used. These samples were placed inside a 2500 cubic centimeter cylinder and agitated with a mechanical agitator. The mechanical agitator had a speed range of up to 7000 rpm. An initial wetting time of 10 minutes was considered enough to wet all the particles within the suspension. Various possible reagents were screened. After the reagent addition the slurry was conditioned for another 4 minutes. Of the various agglomerating reagents tested and from the results in Table 2, crude oil was chosen, because of its abundance and cheap price to be used in the subsequent experiments. The slurry agitated with a speed of 3500 rpm, and the whole content of the cylinder was passed through a 106 micrometer sieve and the agglomerates, remaining inside the sieve, were then washed under the tap, collected, dried and prepared for ash analysis.

Crude Oil Dosages Spherical oil agglomeration screening tests for an artificial

TABLE 3. The Effects of Crude Oil Dosage (g/50 g Feed Coal) on Agglomerates Ash Content (% wt), Grade (%), and dmmf Coal Recovery (%).

Crude Oil Dosage (gr/50gr Feed Coal)	Agglomerates						
	wt of Aggl. (gr)	Ash in Aggl. (wt%)	wt Dmmf Coal in Aggl.(gr)	Grade (%)	Reco of Dmmf Coal(%)	Oil with Aggl. (gr)	Water with Aggl.(gr)
0.843	9.61	12.51	8.42	40.43	5.65	21.29	0.168
1.69	14.32	10.50	12.81	50.00	5.33	32.45	0.498
2.53	19.29	9.60	17.44	54.29	44.15	0.973	5.21
3.37	19.70	8.80	17.97	58.10	45.48	1.092	4.96
4.22	20.35	8.50	18.62	59.52	47.14	1.532	4.64
5.06	21.19	9.00	19.28	57.14	48.82	1.893	4.37
5.90	22.18	8.50	20.29	59.52	51.34	2.328	4.22
6.74	24.46	8.00	22.50	61.90	56.97	2.962	4.27
7.59	25.30	8.50	23.15	59.52	58.61	.352	3.96
8.43	25.35	8.00	23.32	61.90	59.04	3.588	3.67
10.96	25.29	8.00	23.27	61.90	58.90	5.107	2.78
12.65	25.38	7.48	23.48	64.38	59.45	5.915	2.43
15.17	25.17	8.20	23.11	60.95	58.50	4.990	2.58
16.86	24.35	9.50	22.04	54.76	55.79	3.947	2.77
25.29	20.02	11.60	17.70	44.76	4.63	44.80	2.020

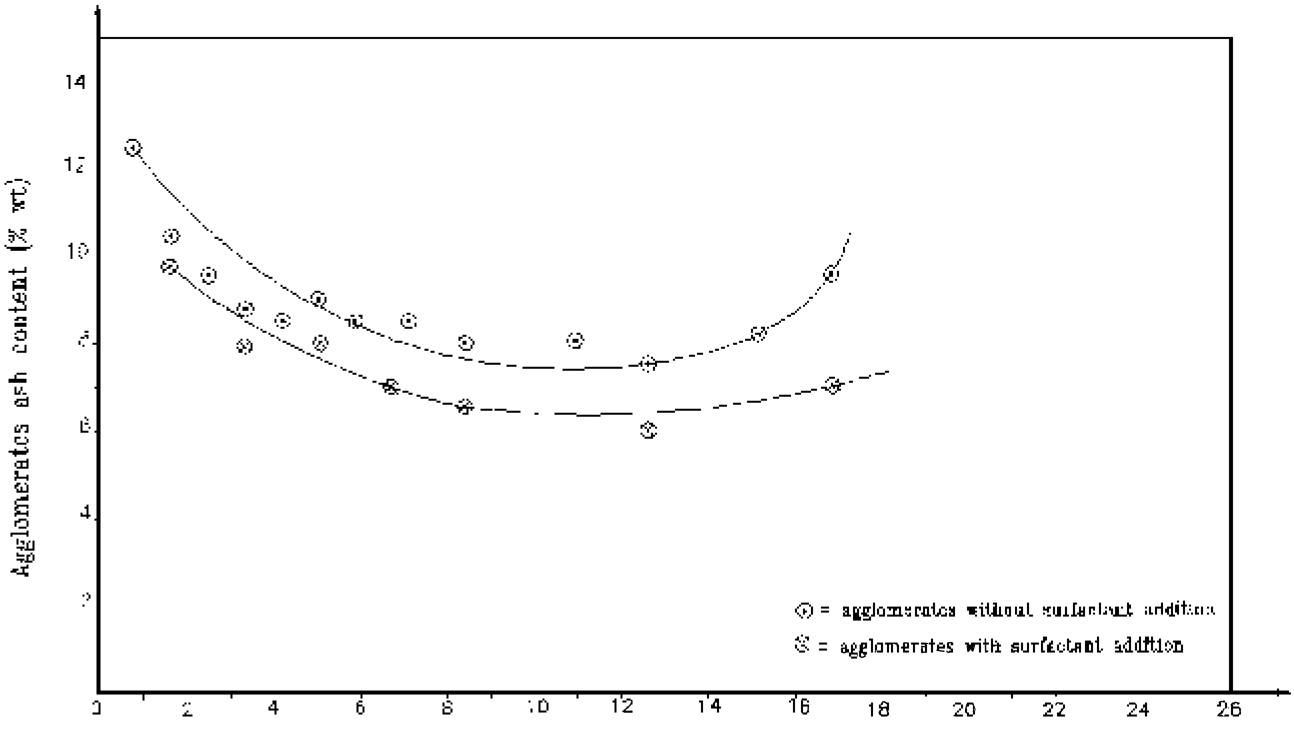

Figure 1. Effects of crude oil addition on agglomerates ash contents (wt%).

TABLE 4. The Effect of Various Surfactants on Ash Content (% wt), Grade (%), and Dmmf Coal Recovery (%). Experimental Condition: Crude Oil Dosage = 12.65 gr to Each 50 gr Reed Coal.

Surfactant Type	Surfactant Dosage (gr/50 gr Feed Coal)	Agglomerates wt of Aggl. (gr)	Ash in Aggl. (wt%)	wt of Dmmf Coal in Aggl. (gr)	Grade (%)	Reco. of Dmmf Coal (%)
Anionic	0.0010	28.04	12.5	24.53	40.48	62.11
Sodium	0.0025	26.62	10.5	23.82	50.00	60.32
Lauryl	0.0250	24.37	9.0	22.18	57.14	56.14
Sulfate	0.075	18.07	10.5	16.17	50.00	40.94
Cationic	0.0050	29.03	13.5	25.11	35.71	63.57
Tetradecyl	0.0500	27.70	12.0	24.38	42.86	62.76
Trimethyl	0.2500	30.37	12.0	26.73	42.86	67.66
Ammonium	0.5000	33.64	16.0	28.26	23.81	71.54
Bromide	1.0000	17.33	18.3	14.16	12.86	35.84
Non-ionic	0.0005	27.84	12.0	24.50	42.86	62.02
Triton	0.0025	29.41	6.5	27.50	69.05	69.61
x-405	0.0570	25.60	7.0	23.81	66.67	60.27
	0.1140	22.46	7.0	20.89	66.67	52.88
	1.1400	17.89	6.5	16.73	69.05	42.35
	3.4200	8.05	6.0	7.57	71.45	19.16
Cationic	0.0010	28.21	11.0	25.11	47.62	63.56
Cetyl	0.0020	29.00	10.5	29.96	50.00	65.71
Trimethyl	0.1010	31.05	12.0	27.32	42.86	69.17
Ammonium	0.2010	33.76	17.0	28.02	19.05	70.94
Bromide	68.94	0.4000	33.01	17.5	27.23	16.67
Anionic,	0.0010	21.82	18.5	17.78	11.90	45.02
Oleic	0.0420	30.34	13.0	26.40	38.10	66.82
Acid	0.0890	29.62	14.0	25.47	33.33	64.49
Creosote	0.0255	30.02	13.5	25.97	37.71	65.74
	0.0510	30.47	12.0	26.81	42.86	67.88
	0.0100	22.89	9.5	20.72	54.76	52.44
Non-ionic	0.0025	23.24	9.5	21.03	54.76	53.25
Hexan-1-ol	0.0500	29.88	9.5	27.04	54.76	68.46
	0.4000	18.03	11.4	15.97	45.71	40.44

mixture of coal/shale, produced agglomerate swith significantly lower ash contents. In order to see whether the same effect could be observed on a Run-of-Mine (R.O.M) coal subsequent experiments were carried out on Run-of-Mine (obtained from British Coal Board Headquarters, Bretby, UK). The effect of varying the agglomerating reagent dosage on the ash content of the agglomerates after washing and drying are presented in Table 3 and shown in Figure 1.

Determination of Grade and Recovery The ash contents (% wt) of the agglomerates were measured according to the procedures in BS 1016: part 3: 1973.

The grade [G(t)] and the recovery [R(t)] were determined according to the definitions given below:

$$G(t) = \left[1 - \frac{Xc(t)}{Xf} \right] * 100 \qquad (1)$$

$$R(t) = \left\{ C(t) \left[1 - \frac{Xc(t)}{F(1-Xf)} \right] \right\} * 100 \qquad (2)$$

Surfactants Screening Spherical oil agglomeration techniques have not been fully commercialized due to the necessity of high usage of agglomerating reagent. It was later discovered that the reagent usage can considerably be reduced by the addition of certain surface active chemicals [5]. To a 10% by weight Run-of-Mine coal suspension various surfactants at different concentrations were added.The surfactants were added to the suspension after two minutes of wetting and the slurry was further conditioned. 12.65 g normal crude oil was added to each 50 g of dry feed and after 3 more minutes (altogether 5 minutes of agglomeration time) the agglomerates were recovered and analysed for their ash content, grade and dmmf (mineral matter free) coal recovery. The results of the screening tests are given in Table 4. Of the various surfactants screened Triton x.405, a non.ionic aqueous surfactant, produced agglomerates with the lowest ash contents. The ash contents of the washed agglomerates are presented in Table 5 and shown in Figure 1. The optimum dosage was 0.0025 g/50g of coal.

Other Variables Determined Other variables studied included solids concentration, agglomeration time, agitation speed, emulsification effect, solids wetting time and the effects of slurry pH on agglomerates ash content.

DISCUSSIONS

Oil Type and Concentration Variations in demineralization due to different additions of the agglomerating reagent were to be expected. From the results obtained by various researchers [4,5] on an artificial coal/shale mixture, the economics of the process using diesel oil, is less attractive than crude oil because of its higher price and less availability.

In contrast to Blaschke's [4] findings, diesel oil did not produce low ash content agglomerates. This agrees with the findings of Capes et al [9], who believes diesel oil because of its low density and viscosity, does not hold the coal particles together and the agglomerates formed are of the primary type which due to their small size and weak nature, will rupture, on agitation and subsequently pass through the openings of the sieve.

Therefore, the crude oil (obtained from The North Sea) because of its medium density and surface tension and its ability to agglomerate more coal particles than the diesel oil was preferred as an agglomerating reagent. Another important factor regarding the economics of the use of the crude oil is its lower price compared to the other reagents.

At 12.65 g crude oil to each 50 g feed coal, agglomerates with ash contents of 7.5% by weight together with combustible recoveries of 60% were obtained. At this value the agglomerates retained the highest amount of the reagent and the lowest amount of moisture (Table 3 and Figure 2). With this crude oil dosage the maximum carbonaceous constituents (hydrophobic particles) are retained while the noncarbonaceous materials (hydrophilic particles) are rejected with the water.

Surfactant Concentration De-sliming is an important step in any efficient ultrafine coal processing. To reduce the high crude oil addition a non-ionic surfactant, Triton x-405, was added after screening tests.

It is generally believed that non-ionic surfactants exhibit some anionic characteristics. When added to the suspension they coat the noncarbonaceous particles and decrease their

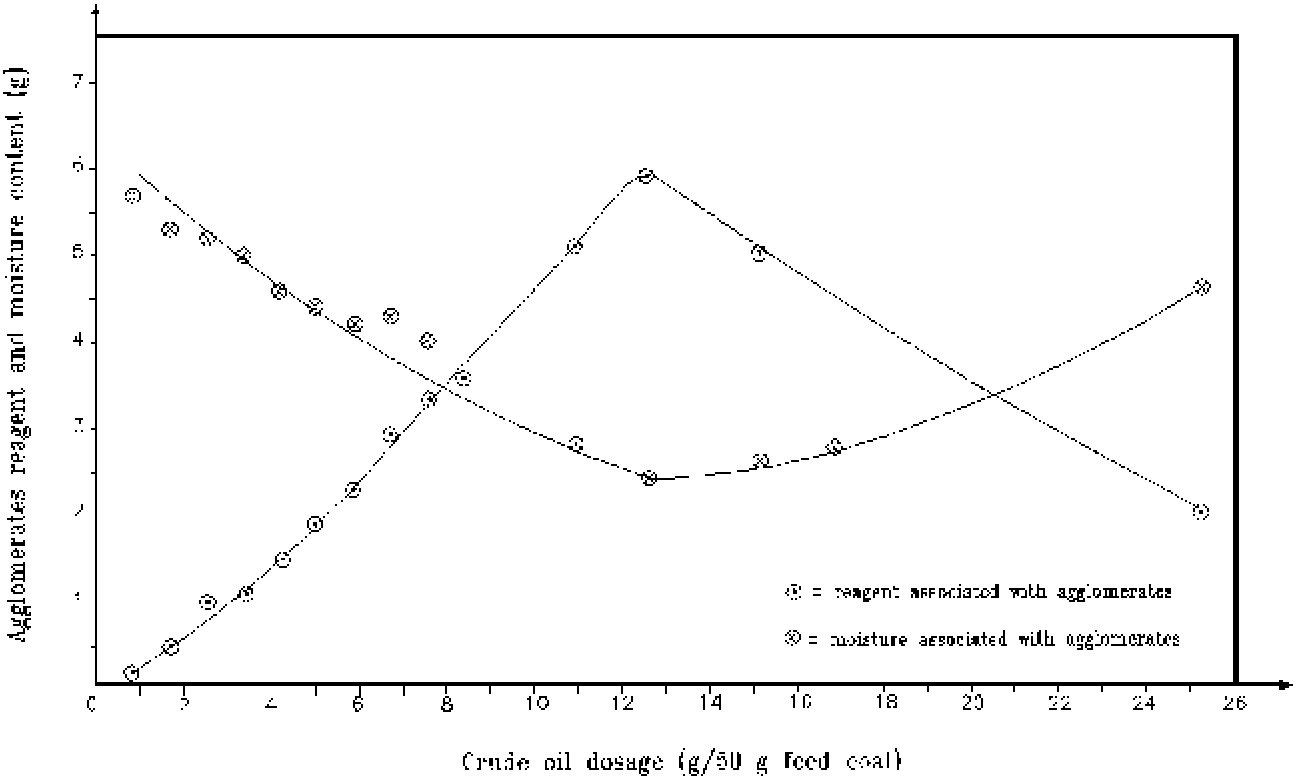

Figure 2. Effects of crude oil addition on agglomerates ash contents (wt%).

TABLE 5. The Effects of Triton x-405 (Non-Ionic) and Crude Oil Dosage on Ash Content (% wt), Grade (%), and Dmmf Coal Recovery (%).

Experimental condition: Surfactant Dosage = 0.0025 g/50 g Feed Coal

Crude Oil	Agglomerates				
Dosage (gr/50 gr Feed Coal)	wt of Aggl. (gr)	Ash in Aggl. (wt%)	wt of Dmmf Coal in Aggl. (gr)	Grade (%)	Reco. of Dmmf Coal (%)
1.686	16.45	9.8	14.84	53.33	37.56
3.372	20.23	8.0	18.61	61.90	47.12
5.058	22.83	8.0	21.00	61.90	53.17
6.744	26.48	7.0	24.49	64.29	62.01
8.430	27.33	6.5	25.55	69.05	64.69
12.65	29.62	6.0	27.84	71.43	70.45
16.86	26.80	7.0	24.92	66.67	63.10

zeta potential [10]. This is a likely reason for the reduction of ash within the agglomerates. In this series of experiments Triton X-45 at 0.0025 g/50g of coal was found to give optimum results.

TABLE 6. The Effect of Agitator Speed (rpm) on Ash Contents (wt%), Grade (%) and dmmf Coal Recovery (%).

Agitator Speed (rpm)	Agglomerates				
	wt of Aggl. (gr)	Ash in Aggl. (wt%)	wt of Dmmf Coal in Aggl. (gr)	Grade (%)	Reco. of Dmmf Coal (%)
1200	24.65	9.38	22.31	55.33	56.55
2000	25.09	8.11	23.06	61.38	58.38
3500	25.41	7.80	23.43	62.86	59.31
4000	25.50	7.82	23.51	62.76	59.51
5100	25.19	7.90	23.20	62.38	58.73
5700	24.30	8.14	22.32	61.24	56.51
6600	23.47	10.32	21.05	50.86	53.29

Solids Concentration Solid concentrations between 5 to 30% by weight have been examined [10].The lowest ash content agglomerates were obtained when a solid concentration of around 10% by weight was used. This was probably because at low solid concentrations the number of particle-oil collisions is low and some of the oil droplets never meet the solid particles and leave the process unaffected.

At medium solid concentrations it seems that the optimum collisions between the oil droplets and the solid particles occur. At these critical solid concentrations the usage of oil and coal particles balance.

At concentrations higher than the optimum there are not enough oil droplets to cover all the solid particles and leaving some of the coal particles untreated which leave the system in the waste stream.

Agglomeration Time An agglomeration time of around five minutes produced comparatively strong and low ash agglomerates. At lower agglomeration times the immiscible liquid is not completely dispersed and consequently not all the hydrophobic coal particles are collected by the oil droplets. Longer agitation times produced agglomerates with high ash content. This possibility follows that once all the carbonaceous constituents have been contacted by the reagent some of the gangues may also be trapped within the agglomerates.

Agitator Speed Vigorous agitation is needed firstly to keep all the particles suspended and secondly to create enough momentum for the particles to intercept the oil droplets. At this initial stage the primary agglomerates are one-dimensional, floc-types, and are very weak and voluminous. If the agitation speed and time are not well balanced then these weak agglomerates will break down on sieving. If the speed and the agglomeration times are satisfactory two-dimensional, strong agglomerates are produced which can withstand washing. Higher speeds will probably break the agglomerates. This will result in a loss of carbonaceous content of the suspension with the least chance of reform. The results are given in Table 6.

CONCLUSIONS

Significant ash reductions were achieved with Spherical Oil Agglomeration techniques which are consistent with the findings of various authors [6,7,8,9] at oil to coal ratios of 0.25 to 1.0 by weight. These agglomerates were strong enough to be separated from the suspension by sieving. By using surface active agent, Triton x.405, at concentration of 0.0025 g to each 50g feed coal, over 60% reduction in weight of the crude oil usage, and concentrates ash levels of 8% by weight were achieved. This is an improved technique compared to that of the Abdulrahman et al [5] which could only reduce the oil usage by 20% by weight. The amount of the reagent retained with the agglomerates will pay for the price of the surfactant used.

ACKNOWLEDGEMENT

The author gratefully acknowledge the moral and the financial assistance received from the Ministry of Culture and Higher Education in Iran and the Chemical Engineering Department at UMIST, England.

NOMENCLATURE

F = mass of dry feed (g)

G(t) = grade (%)

R(t) = recovery (%)

$X_c(t)$ = fractional ash content of the cumulative concentrate at the time t

X_f = total ash content of the feed

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