

REMOVAL OF HMW ORGANIC COMPOUNDS BY PARTIAL WET OXIDATION

B. J. Foster and M. L. Roberson

Kaiser Aluminum & Chemical Corporation
P. O. Box 337
Gramercy, LA. 70052ABSTRACT

Since the late 1970's, extensive testing has been conducted at Gramercy to remove high molecular weight organic compounds (humates) from Bayer process liquors. Early research work tested the removal of humates using the Giulini process (Dolime), and by the use of organic polymeric additives.

This paper will present another method that has been developed to remove humates from Bayer process liquors. In this method, the desired humate destruction is accomplished by introducing in the Bayer process liquor only as much oxygen as is soluble in the liquor under the particular processing conditions. The solubility limit of oxygen in the liquor is never exceeded. This process avoids the use of temperatures which are above the conventionally employed range, avoids the use of catalysts and large quantities of oxygen or air, accomplishes humate destruction well within the time available in the digestion stage of the Bayer process, and makes use of existing process equipment.

INTRODUCTION

The Gramercy Alumina Plant is an 800,000 MTPY plant located in Gramercy, Louisiana. The plant was originally constructed in the late 1950's as a high temperature monohydrate process plant. The plant was modified in the 1960's to a close-coupled sweetening process and subsequent productivity expansions have increased its capacity to its present rate. The plant processes North Coast Jamaican Bauxite.

Beginning in the early 1980's, laboratory studies confirmed published works by others (Giulini) that, under certain conditions, the removal of humates from process liquor could have a positive effect in the particle size control of the precipitation process. Therefore, process conditions could be altered, thereby increasing the productivity (yield) of the plant. Based on this information, a full-scale plant test using the Giulini process was conducted. The humate concentration in the plant liquor was reduced. However, the incremental productivity increases did not off-set the additional processing costs.

Although the Giulini process was not cost-effective for Gramercy, the results were encour-

aging. Kaiser entered into a joint research agreement with Nalco Chemical Company to develop an alternate approach to humate removal. After extensive laboratory research and plant tests, the process was perfected. U. S. Patent 4,578,255, Purification of Bayer Process Liquors, Roe and Malito, describes in detail this process. For Gramercy, this process was not sufficiently cost effective. The humate value for Gramercy liquor is considered "not high" compared to other plants; i.e., the normal concentration of humates in Gramercy liquor is slightly less than the humate concentration of the liquor in plants that are successfully using the above process. Meanwhile, research continued into alternate processes that could result in a cost effective approach to humate reduction and subsequent yield improvement. The end-product of this research is described in U. S. Patent 4,663,133, Removal of High Molecular Weight Organic Compounds from Bayer Process Liquor, Malito and Roberson, Kaiser Aluminum & Chemical Corporation. Full scale plant tests have confirmed the results of the research work described in the patent.

The paper will review the concepts of the partial wet oxidation process, and the results obtained in the full-scale plant tests.

PROCESS DESCRIPTION

Caustic Bayer process liquors, contaminated with humate impurities, are treated with oxygen under conventional digestion conditions by limiting the oxygen quantity added to the liquor to such an amount which is at or below the solubility limit of oxygen in the liquor under the particular processing step. By controlling the oxygen quantity as set forth, excessive pressures and temperatures can be avoided while simultaneously most of the humate impurities can be destroyed within normal digestion times at a significantly reduced oxygen consumption.

Brief Description of the Figures

Figure 1 shows the solubility of oxygen in a caustic aluminate liquor at constant caustic concentration and at varying temperatures in a closed system.

Figure 2 shows the relationship of humate destruction (as measured by light absorbance dif-

ference) versus reaction time at 243°C. digestion temperature and at 0.8 g/L oxygen charge.

Figure 3 depicts the relationship of humate destruction (as measured by light absorbance difference) versus reaction time at 200°C. preheating temperature and at 0.5 g/L oxygen charge.

Figure 4 demonstrates the effects of varying oxygen quantities (all within the equilibrium solubility limit) on humate destruction at 200°C. versus reaction time.

Figure 5 schematically shows the predigestion and digestion stages of the Bayer process with dotted lines indicating suitable areas where oxygen can be added to the system for humate removal.

The terms "caustic Bayer liquor" or "caustic liquor" refer to alkaline process streams utilized in the processing of bauxite to alumina trihydrate.

These process streams include the liquor used to digest bauxite, the pregnant liquor obtained as a result of digestion and the spent liquor which is depleted in alumina content due to precipitation. An A/C ratio generally from about 0.30 to about 0.72 illustrates the range from the most dilute to the most concentrated caustic liquor employed in the Bayer process.

The terms "oxygen solubility" and "equilibrium oxygen solubility" as used herein refer to the quantity of oxygen, expressed in grams which dissolves in a liter of caustic liquor under the process conditions used for humate removal from Bayer liquors. The pertinent process parameters include temperature and pressure and also the caustic concentration of the liquor expressed in grams per liter as Na_2CO_3 . The internal pressure in digesters, heaters, and associated equipment is normally maintained at levels greater than the vapor pressure of the liquor within these vessels, so that the solubility of oxygen is enhanced.

For most plants employing the Bayer process for the production of alumina trihydrate from bauxite sources, the humate removal process can be advantageously utilized in the predigestion stage and/or in digestion. The predigestion stage generally involves the preheating of the caustic liquor and/or caustic liquor-bauxite slurry up to digestion temperature prior to digestion. It may also include a desilication step, which is utilized to react and precipitate a portion of the silica content of bauxite prior to digestion. The humate removal process can be applied in these predigestion stages provided the temperature and/or pressure is sufficiently high to provide a reasonably fast rate of reaction between the dissolved oxygen and the humate content of the liquor. Since digestion of the bauxite usually takes place under elevated temperature and pressure conditions, a fast rate of reaction between the oxygen and the humate impurity is assured.

It has been found that in order to assure an acceptable rate of humate removal by oxidation the temperature of the treatment should be at least about 200°C., preferably not less than about 140°C.

The upper limit of the treatment temperature is generally established by the conditions set for the particular Bayer process operation, for example the conditions existing in the preheating, desilication or digestion steps. Since the instant humate removal process uses oxygen only up to a quantity which dissolves in the liquor, oxygen will contribute very little to the total pressure of the system, which will be determined mainly by the vapor pressure generated due to the temperatures existing in the treatment vessels, and by the overpressure afforded by the various feed pumps.

Introduction of oxygen for humate removal according to the invention can be accomplished as mentioned before, in the liquor and/or slurry preheating stages, during the desilication step or in the digestion stage. Since the rate of humate removal is dependent on the temperature, it is preferred to employ the oxygen only in such treatment vessels where the temperature is at least about 100°C. Thus, in the liquor or slurry preheating stage, which generally utilizes two or more preheating vessels, as is also shown in Figure 5, the oxygen should be introduced only into one of those vessels in which the temperature is at least 100°C. In the predesilication stage, which is utilized by some Bayer process alumina production facilities, the instant humate removal process can be advantageously applied provided the temperature in the predesilication stage is in excess of 100°C. Naturally, since digestion of bauxite is accomplished at temperatures in excess of about 140°C., the instant humate oxidation process can be readily employed in the digestion stage.

The humate constituent of the total organic impurity content of bauxites is very small, generally about 5-15% by weight of the total organic carbon content. Consequently, the quantity of oxygen to be employed for the oxidative destruction of the humate is also very small, since the total organic content of bauxites is generally less than about 0.2% by weight of the bauxite. It has been found that to effect satisfactory humate removal from the liquor or slurry, the quantity of oxygen capable of remaining in solution at the treatment temperatures utilized is sufficient to oxidize the humate content. For practically all bauxites, the quantity of oxygen which is capable of dissolving in the liquor or slurry is more than enough to control the humate content in liquor to low and satisfactory levels. Thus, in batch processes, a single introduction of the equilibrium solubility quantity of oxygen is sufficient, while in continuous or semicontinuous preheating, desilication or digestion processes, the required quantity of oxygen is charged in relation to the rate of introduction of humates into the process vessels.

As it has been mentioned before, the quantity of oxygen which dissolves in the liquor or slurry depends on the temperature of these process streams. Table I below illustrates the quantity of oxygen which is capable of dissolving in a caustic liquor having a caustic concentration of 250 grams/liter (calculated as Na_2CO_3) at varying temperatures. The temperature-dissolved oxygen re-relationship is also shown graphically in Figure 1.

Table I. Oxygen Solubility in a Caustic Liquor As a Function of Temperature*

Temperature in °C	Dissolved Oxygen Content O ₂ , grams/L Liquor
77°	0.18
120	0.23
146°	0.25
166°	0.44
186°	0.55
211°	0.63
237°	0.83
253°	1.04

*Caustic conc. = 250 g/L.

Considering the bauxites generally contain less than about 0.2% by weight organic carbon and only about 5-15% of such organic carbon can be attributed to the humate content, it becomes readily observable that, even at about 100°C, the dissolved oxygen content of the liquor is more than sufficient to oxidize the humate constituent of the liquor. Due to the small quantity of oxygen required for humate removal, the introduction of oxygen into the process vessels can be easily and economically accomplished without the necessity of using special high pressure transfer equipment, for example pumps modified for oxygen introduction. The present humate removal process allows the direct introduction of oxygen from oxygen storage vessels, which contain compressed oxygen. Other advantages of the instant humate removal process are readily observable from the examples presented hereinafter.

Example 1

Batch digestion of Jamaican bauxite was carried out with simultaneous destruction of its humate content. The bauxite composition is shown in Table II.

Table II. Jamaican Bauxite Composition

Component	% By Weight (Dry Basis)
Al ₂ O ₃	47.6-48.8
SiO ₂	0.6-1.0
Fe ₂ O ₃	17.9-18.4
Organic carbon as C	0.15-0.25
Humate carbon as C*	0.009-0.02

*Determined by absorbance

The bauxite was slurried in caustic liquor and the slurry had an A/C ratio of 0.411 and a caustic concentration of 242 g/L. This slurry was charged to the digester and heated to 243°C. When the slurry reached the desired temperature, 0.5 g/L O₂ was charged to the digester from a cylinder containing compressed oxygen. This quantity of oxygen was significantly less (0.5 g/L v. 0.9 g/L) than the quantity that is capable of dissolving in the slurry at the digestion temperature utilized. The course of humate destruction was followed by measuring the change in the color of the slurry through colorimetric means. The colorimetric means utilized was a Pye Unicam Model 6-350 spectrophotometer

and the light absorbance change was measured at 691 nm in a 4 cm cell. Calibration of the instrument was accomplished by using a humate standard. Table III presents the rate of humate removal as a function of time under the digestion conditions described and the results are also graphically shown in Figure 2.

Table III. Humate Destruction in Digestion

Time In Minutes	Absorbance (At 691 nm)	Humate Destruction in %
0	0.304	0
2	0.235	22.7
16	0.152	50.0
26	0.137	54.9
40	0.130	57.2
60	0.123	59.5

Example 2

Humate removal was accomplished during the preheating of Bayer process (test tank) liquor. This liquor, when preheated to digestion temperature, is then combined with bauxite slurry and the combined liquor-bauxite slurry composition is subjected to digestion. The test tank liquor utilized in this example had been previously subjected to several Bayer process cycles and as a result had a dark red color due to the high dissolved humate content. This caustic liquor had a caustic concentration of 225 g/L and was introduced into the preheating stage of the Bayer process. The preheating stage, as shown in Figure 5, consisted of several preheating vessels connected in series and the liquor was preheated in stages. Since the rate of humate oxidation is dependent on the temperature, oxygen was introduced to a specific preheating vessel where the test tank liquor temperature was to be raised to about 200°C. At this temperature, the oxygen equilibrium solubility equals about 0.60 g/L at the given caustic concentration; however, only 0.50 g/L oxygen was charged. The humate destruction was followed by absorbance measurements, and the results were tabulated as a function of time and are shown in Table IV and are also graphically depicted in Figure 3.

Table IV. Humate Destruction in Preheating

Time In Minutes	Absorbance (At 691 nm)	Humate Destruction in %
0	0.350	0
2	0.267	23.7
7	0.212	39.4
16	0.162	53.7
26	0.141	59.7
40	0.129	63.1
60	0.122	65.1

It can be observed that when only about 80% of the quantity of oxygen is supplied of the total capable of being dissolved in the caustic liquor, more than 50% of the total humate content can be readily destroyed in less than about 15 minutes. Longer residence times, coupled with addition of oxygen up to the equilibrium solubility limit at

the given temperature, can significantly increase the degree of humate destruction.

Example 3

Tests were conducted to establish the effect of varying oxygen quantities on humate destruction at a constant temperature and at a preselected caustic concentration. Thus, humate-containing spent liquor, obtained from the precipitation stage of the Bayer process after removal precipitated alumina trihydrate from it, was subjected to the humate destruction step of the instant process. The spent liquor had an A/C ratio of 0.342 and a caustic concentration of 225 g/L. Humate destruction was carried out at 200°C. by charging varying quantities of oxygen to the liquor sample up to the limit of oxygen solubility under the test conditions. It was found that considerable humate destruction can be achieved even if only one-half of the total oxygen capable of remaining dissolved in the spent liquor is charged to the liquor. Table V provides the results in tabulated form, while Figure 4 graphically shows the same.

Table V. Humate Destruction
as a Function
Of O₂ Quantity

O ₂ in g/L	Time in Minutes									
	0	5	10	15	20	25	30	35	40	
	Absorbance at 691 nm									
.1	.376	.340	.332	.330	-	-	-	-	-	-
.2	.376	.306	.291	.286	-	-	-	-	-	-
.3	.376	.276	.252	.244	.240	-	-	-	-	-
.4	.376	.252	.222	.208	.202	.198	.196	.194	-	-
.5	.376	.228	.192	.176	.166	.160	.156	.156	-	-
.6	.376	.218	.170	.150	.138	.130	.124	.120	.116	-
.7	.376	.192	.150	.128	.115	.107	.100	.094	.090	-

*At 200°C. and 225 g/L caustic concentration.

It can be observed that the very small quantities of oxygen utilized can accomplish substantial reduction in humate content within reasonably short reaction times. Due to these small oxygen quantities employed, the present humate removal process does not require extensive oxygen charging equipment; in most instances the oxygen can be directly charged from vessels containing it under compression. Also, by using these small quantities, one does not encounter the serious corrosion problems of the prior art wet oxidation processes.

PLANT TESTS

Summary

Gaseous oxygen injection to the thick slurry pretreat vessel started on September 17, 1985, and continued until February 11, 1986, when it was shut down. Injection was continuous during this period, except when interrupted by digestion equipment outages, or pretreat vessel inspections. Injection rates varied from 4-8 tons/day oxygen, with pretreat temperatures varying from 430-460°F.

At an average rate of 4 tons/day, oxygen injection was found to block incoming humates with the bauxite, as measured by liquor absorbance in the pretreater effluent. Under Gramercy conditions

about half of the injected oxygen went to oxidizing sodium thiosulfate to sodium sulfate. The rest reacted with humates.

Beneficial effects of wet oxygen were an improvement in hydrate reflectance and a reduction in sodium aluminate insolubles. The oxalate to caustic ratio in liquor to precipitation fell from 0.012 to 0.008. The humate level was also reduced by 33%.

Process and Facilities

Supply of gaseous oxygen was from portable facilities, provided by Airco, consisting of cryogenic liquid storage, pump, vaporizers, and high pressure gas storage.

The O₂ was is metered into the No. 1 Desilicator slurry using a steam carrier for dispersion via 1" Stainless Steel line to an existing nozzle on the 3rd platform level. Monel pipe was used internally. An automatic vent system was installed on the vessel to prevent gaseous oxygen from building up in dome, particularly during upset conditions. The vent discharged to a flash pot located on the ground floor near the slurry mix sump which received the drainage. Provision for venting was more precautionary than necessary. In operation, no oxygen or other gas was ever detected at the top of the vessel, indicating complete oxygen dissolution. The instrument control scheme allowed for automatic venting of the vessel and shut-off of the oxygen feed in the event of a loss of liquid level control in the vessel.

It was expected that steam dispersion of the oxygen into the agitated mass of pretreat slurry about 30 feet below the vessel dome would result in rapid solution and reaction. However, as a precaution against the possibility of corrosion, the entry stage of the vessel and the one about it was lined with 1/4" steel plate. Inspections at 1 and 4 month intervals showed no evidence of oxygen attack.

A sample point was provided at the exit of the pretreater before the treated liquor was mixed with the main spent liquor stream so that more direct measurements could be made of treatment effectiveness.

System Operation and Results

The system installed permitted a maximum sustained injection rate of about 8 tons/day oxygen. Operation averaged 4 tons/day, sufficient to block fresh humate input to the plant.

Reliability of the oxygen system was good. There was one O₂ pump failure and two instances of flow interruption due to trash in the suction screen.

AIRCO recommended a larger pump and larger liquid oxygen tank for a permanent installation to give higher injection rates.

The corrosive effects of oxygen were a major concern. The vessel was inspected twice with no visible evidence of corrosion to the vessel or its internals. The agitator shaft at the stuffing box shows no evidence of corrosion or pitting.

Hydrate Reflectance. Hydrate reflectance increased to 77-80%, up from previous levels of 68-74%, and then declined to about 75% when oxygen was cut off.

Sodium Aluminate. There was an improvement in color and a reduction in insols during oxygen addition. The effect of an oxygen outage was seen within a few days as a return of sodium aluminate quality to previous level.

Precipitation Yield. No measurable increase in yield was seen, with the exception of a brief, not sustained improvement in granulometry in October. To an observer unaware that O₂ was being added to the system, looking only at precipitation chemistry and granulometry, it would not be obvious that a change had occurred elsewhere in the system. There were observable changes in ST seed oxalate. Analysis of data shows that the large variations in seed oxalate started in June, the month after DADMAC addition ceased, and two months before O₂ addition. The variation was about normal in January.

Liquor Purity. With the exception of a reduction in soluble oxalate to caustic ratio from 0.012 to 0.008 and a reduction in absorbance, there has been no clear change in liquor purity. Variations are within the range of historical data.

Tables VI and VII show liquor absorbance to caustic ratios and selected liquor analyses for the period.

Table VIII shows S.T. seed oxalate variability.

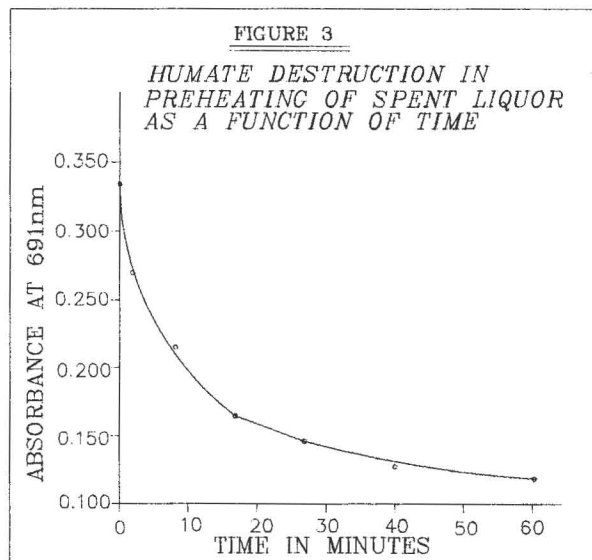
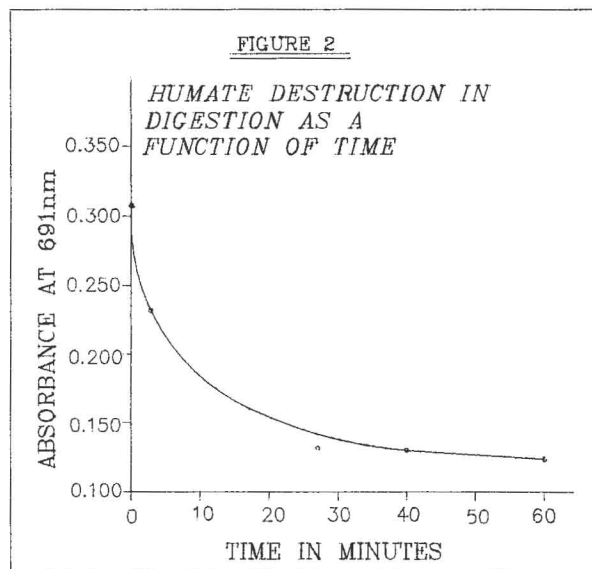
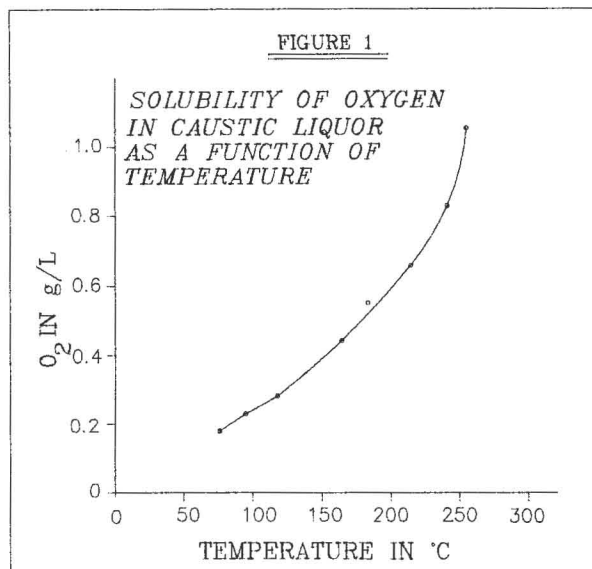
Table IX shows the distribution of simple organics in the liquor compared to other KACC-affiliated plants.

Oxygen Consumption. Gramercy liquor contains both sodium sulfide and thiosulfate. Both species are attacked by oxygen, and these reactions account for 1/3 to 1/2 of the oxygen consumed in the pretreater. These reactions appear to be concurrent with humate oxidation. From plant tests, about 0.06 tons of humate carbon are destroyed per ton oxygen injected.

CONCLUSIONS

Partial wet oxidation proved to be an effective method to remove humates from the Bayer plant liquor. Other problems in the precipitation liquor circuit, notably classification, prevented the precipitation process from being "stressed" during this plant test. As a result of these problems, this method is not cost-effective at Gramercy. It must be noted, however, that for the economics in place at Gramercy, the cost to remove 1 ton of humate by the partial wet oxidation process was substantially less than the organic additive process and the Giulini process.

Whether this process or other humate removal schemes can be cost-effective at other alumina plants will depend on the level of humate contamination, precipitation process and equipment design, and economic considerations.



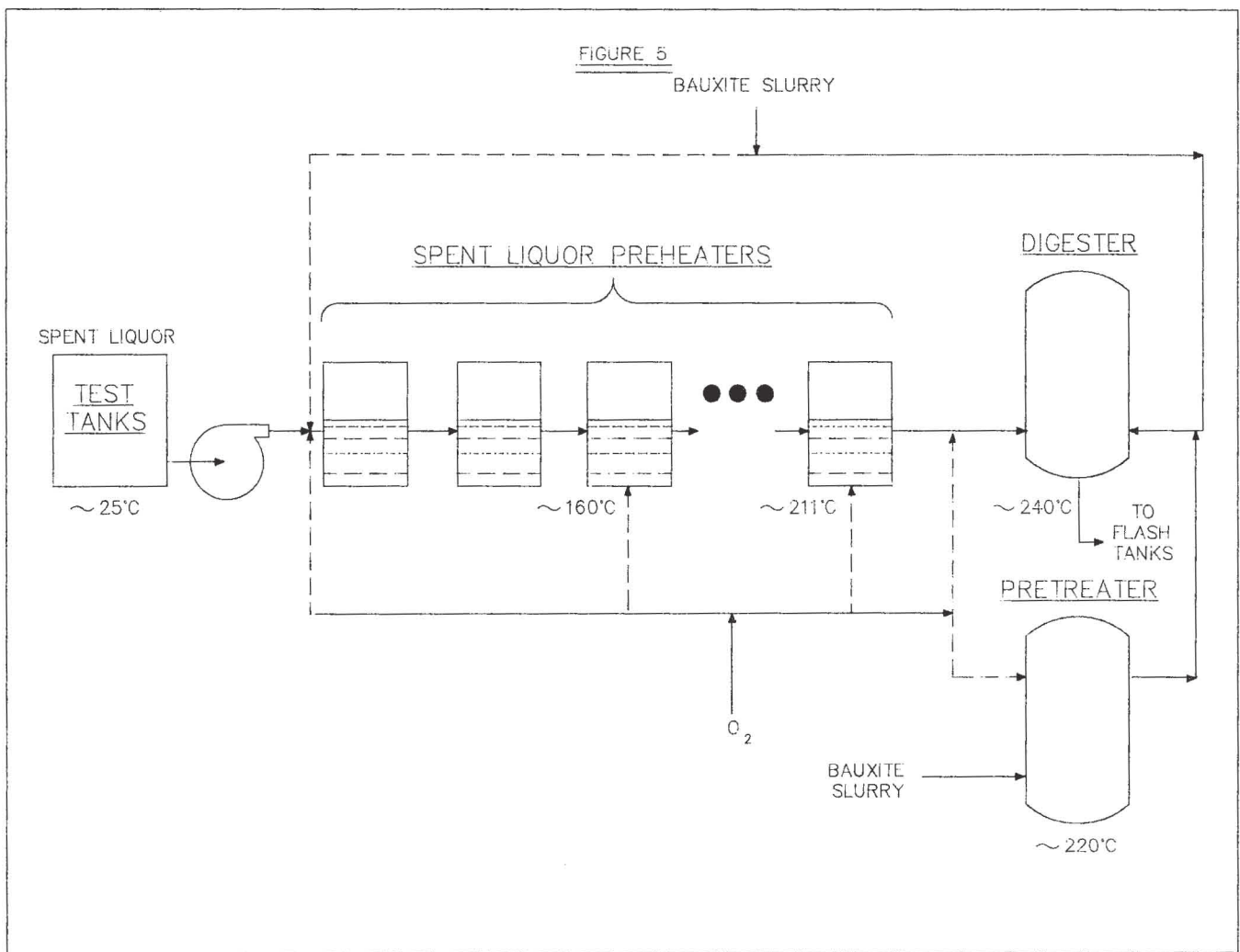
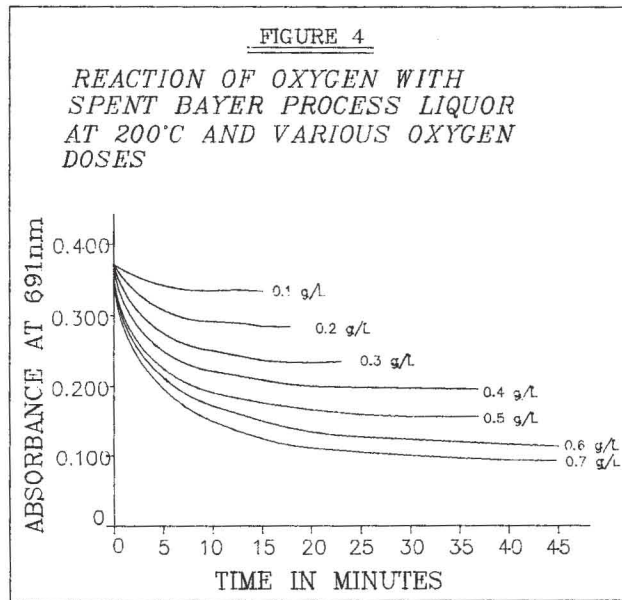


Table VI. Liquid Absorbance
L-P Sample

	Abs/C Ratio (Avg) (x10 ³)	O ₂ Rate, Avg. T/D
July 1985	1.40	0
August 1985	1.20	0
September 1985	1.10	5.27 (17th-30th)
October 1985	1.11	3.94
November 1985	0.75	4.26
December 1985	0.74	3.63
January 1986	0.82	4.11

Table VII. Liquor Analyses

	7-22-85	10-1-85	1-7-86	1-27-86
TOOC/C	0.432	0.380	0.411	0.402
OXS/C	0.012	0.008	0.008	-
C/S	0.816	0.814	0.811	0.807

Table VIII. S.T. Seed Oxalate

Month	Mean	Std. Dev.	Additive Dadmac/ Oxygen
September 1984	0.415	0.152	-
October 1984	0.402	0.108	-
November 1984	0.348	0.080	D
December 1984	0.387	0.067	D
January 1985	0.390	0.059	D
February 1985	0.339	0.080	-
March 1985	0.441	0.065	D
April 1985	0.435	0.137	D
May 1985	0.441	0.156	D
June 1985	0.441	0.145	D
July 1985	0.556	0.415	-
August 1985	0.819	0.372	-
September 1985	0.343	0.288	O
October 1985	0.193	0.167	O
November 1985	0.488	0.180	O
December 1985	0.518	0.395	O
January 1986	0.318	0.134	O

Table IX. Distribution of Simple Organics in
KACC-Affiliated Bayer Plant Liquors

Plant	Sample Date	CS	g/l ONa	TOOC	Carbon No.	Acetate	Formate % of Total Organic Soda	Succinate	Oxalate	
Gramercy	1/86	231	21.9	94.9	4.3	33	15	2	9	59
	5/82	176	28.7	116.5	4.1	34	13	8	10	65
	1/79	189	30.8	117.9	3.8	29	12	8	9	58
Baton Rouge	4/82	237	31.0	119.1	3.8	31	15	6	8	60
	12/79	172	25.5	98.5	3.9	31	10	6	16	63
	8/79	226	41.4	168.1	4.1	30	11	3	14	58
QAL	4/82	211	45.6	226.9	5.0	31	13	9	6	59
	2/80	225	47.0	241.8	5.1	31	12	10	6	59
	11/79	213	46.2	230.7	5.0	33	12	10	6	61
% of Total Organic Carbon										
Gramercy	1/86					30	7	2	4	43
	5/82					33	6	8	5	52
	1/79					30	6	8	5	49
Baton Rouge	4/82		As above			33	8	7	4	52
	12/79					32	5	7	8	52
	8/79					30	5	3	7	45
QAL	4/82					25	5	8	2	40
	2/80					24	5	8	2	39
	11/79					27	5	8	3	43