DISCOLOURATION OF KRAFT PULP MILL EFFLUENT STUDIES AT OPM-AMLAI

- Sharma, G.D.*, Singh, M.M.* and Agarwal, N.R.*

ABSTRACT

At Orient paper Mills, Amlai the mill effluent is segreated into different categories depending upon their quality. The effluents from the Wash Plant and alkali extraction stages of Bleach Plant along with contaminated gland cooling water and minor spillages from the Digester house and Soda Recovery plant are separately diverted together for treatment and is termed as Grade III effluent. It is blackish brown in colour and is non-biodegradable in nature.

This Grade III effluent is treated in a 120 ft. dia. clariflocculator followed by an anaerobic treatment in a lagoon having 20 days retention period. Sufficient quantities of neutrients are added before this treatment for proper seeding. Part of this treated effluent is pumped to the experimental plantations thereafter. The remaining effluent is further treated in aerobic lagoons and stabilized in the Polishing pond having a retention period of about 7-8 days. The total treatment process is being regularly monitered.

It is observed that inspite of such an ellaborate treatment the effluent discharged is having relatively higher BoD and COD and is also coloured. The colour is due to presence of lignin and is also a basic cause for higher BOD and COD characteristics of the effluent. It also creates anaesthetic problem.

Efforts were done by OPM, Amlai R & D Division to study and develop methods for removal of this colouring matter from the effluent and thereby also reduce COD. The paper describes the various methods of treatment with flocculating agents and degrading agents tried at laboratory and plant level. It was found that degradation of colouring matter with Calcium hypochlorite gave very encouraging results.

* *Orient Paper Mills, Amlai.*

INTRODUCTION

Duggal[1] etal have characterised a colour of a Kraft mill effluent. According to them the colour bodies in all the fraction of the effluent contain lignin like colour bodies having a higher density of negative charge. The lignin is an amorphous colloidal compound and is mainly composed of phenylpropane units. The colour can be reduced or eliminated by the following available processes.

A. Coagulation of the colloidal lignin material and then precipatation.

B. Degradation:
   1. By Biological method
   2. By Chemical method.

Extensive work has been carried out with these methods for the removal of colour in this laboratory as well as elsewhere. It will be out of place to briefly review the work.

Subrahmanyan[2] etal have reviewed the treatment method available for colour removal and according to them colour can be removed by coagulating the colloidal lignin with alum, ferric chloride or sulphate, lime and acid.

Physical methods like absorption with activated carbon needs investigation. In this laboratory studies have been carried out to evaluate the use of fly ash, cinder and calcium hypochlorite sludge but the result was not very encouraging.[3].

The biological method available is by treating with white rots fungi like Polyporous, fomes, aspergillus and pencillin. The experiments done are of preliminary nature[4,5,6]. In this laboratory white rot fungi was tried for removal of colour with encouraging results but the main problem was that it could not survive in effluent.

Extensive work has been carried out on the evaluation of the discharges from different operations and are recorded in Table- 1. It is observed that most of the colour is from Caustic extraction stage of bleaching. Calcium hypochlorite treatment on Caustic extraction discharge were investigated with encouraging results in the laboratory stage as well as in the plant scale[7,8] at Orient Paper Mills, Amlai. These results confirm the findings of the Jhaveri etal[9] and Kapoor etal[10].

The action of hypochlorite on lignin like colour bodies may be that of both oxidation and chlorination, however the high pH of hypochlorite suggest oxidation as the primary reaction[11]. The attack of hypochlorite on lignin like bodies is assumed to proceed through phenol ethers attached to the alpha or beta position in the phenylpropanel[12] skelton or through the free phenolic hydroxyl group[13]. The distructive action of hypochlorite on colouring matter is quite profound with a great part of this getting oxidised all the way to carbon dioxide. The sequence of reaction proposed by Rydholm[14] are shown in Figure-1.

LIGNIN REMOVING METHODS

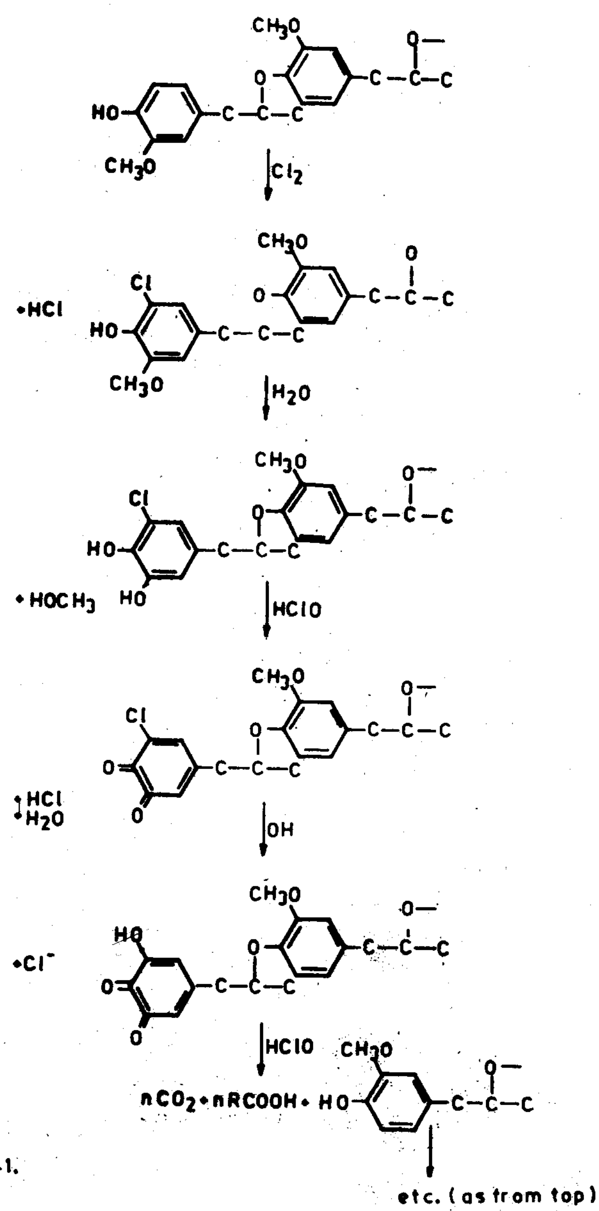

Fig.-1.

The coloured Grade III effluent, discharged from Caustic extraction stage of bleach plant, washing screening drain and contaminated gland cooling water along with occassional spillages from digester house and Soda Recovery Plant was used for these investigation. The physico-chemical characteristics of Grade III waste water are recorded in Table-1. This effluent is having normal pH of 9 to 10.5 and is being adjusted to 8.0 to 9.0 by partial addition of chlorination and hypo stage effluent discharged from bleach plant. The investigation on the removal of colour by both methods viz. coagulation with various coagulating agent and by chemical degradation with hypo chlorite have been carried out at laboratory and plant levels. The results are embodied in this paper.

EXPERIMENTS AND DISCUSSIONS

In the first set of experiments, flocculating agent like alum alone was tried for discolouring the Grade III effluent at different stages of treatment vis - inlet to the clarifier, Anaerobic lagoon 1, outlet and the polishing pond outlet to see where the addition will be more effective. In these sets of experiments 400 c.c. of the effluent was taken and alum in the desired quantity was added. The mixture was agitated at 100 rpm for 10 minutes and at 65 rpm for 10 minutes followed by 10 minutes settling in the laboratory pearl flocculator. The colour, BOD_5, COD, Chloride contents M-Alk as $CaCO_3$ and settlable solid in gm/l were determined by standard method. The results are recorded in Table -2. It is seen that the settleable solids followed by anaerobic lagoon outlet and polishing pond outlet as expected. It is also seen that for the effective colour removal the dose of alum in case of inlet to the clarifier is 800-900 ppm while it is almost the same at Polishing pond outlet. The BOD_5 and COD are also considerably reduced with this addition. The main draw back in this treatment is the removal of the coagulated sludge formed as it is very difficult to separate even in clariflocculator.

In a second set of experiments, efforts were made to reduce the consumption of alum by the addition of Polyelectrolites like P.C. Powder and true flocs S_3. The PC Powder was imported from Japan and was having chain length of aluminium chloride. The addition of alum and the other flocculating agent was done in a similar manner as in the case of alum. True flocs were added before the alum and the results are recorded in Table-3. On scrutiny of the table it is seen that the colour decreases faster with the addition of PC Powder as compared to True floc S or Alum alone. It is also seen that reduction in BOD_5 and COD is not as pronounced as in the case of pure alum but the quantity of alum used is reduced. However, it is observed that the quantity of polyelectrolites required and alum quantity reduced does not compensate each other.

In another set of experiments alum in combination with ferrous sulphate were also tried. The results are recorded in Table-4. It was seen that ferrous sulphate alone is not effective as the focus are not formed and it does not reduce the colour. It is however effective to some extent in combination with alum for colour removal while COD reduction is comparatively lower. In these sets of experiments, it was also observed that pH is lowered and it would be necessary to raise it by addition of Soda Ash etc to bring it to acceptable limits.

Alum in combination with liquid chlorine, waste lime, lime sludge from the causticizer plant and supernatent from lime sludge were also tried. The results are recorded in Table-5. It was seen that chlorine in combination with alum lowered the pH considerably and so it was not encouraging while using it with waste lime and lime sludge the amount of settleable solid was high and the reduction in BOD_5 and COD was not appreciable and so these treatment were not encouraging.

The results of the discolouration of Grade III untreated effluent with calcium hypochlorite alone and in combination with alum, liquid chlorine, and ferrous sulphate are recorded in Table-6. For comparison calcium hypo-chlorite addition was also tried at the aeration pond outlet and the results are also recorded in same table. It is seen from these results that 300 ppm dose of calcium hypochlorite at aeration pond outlet has lowered the colour as well as BOD_5 and COD to an appreciable extent.

From all these results it could be conveniently concluded that the addition of calcium hypochlorite at the inlet of the polishing pond may reduce the colour to an appreciable extent and also reduce the BOD_5 and COD.

To confirm these results addition of 300 ppm of calcium hypochlorite at the inlet of the polishing pond was started in March 1986. The results of untreated and treated Grade III effluent are recorded in Table-7. For comparison previous results from October 1985 are also recorded. It is also reduced to an appreciable extent. It is also seen that except for BOD_5 the effluent discharge meets all the ISI standards 2490.

ACKNOWLEDGEMENT

The authors wish to express their deepest gratitudes to Sri I.M. Bhandari, Executive Vice President, Orient Paper Mills, Amlai for his kind permission to present these findings.

REFERENCES

1. Hardev S.Duggal, Buchanan M.A., Edgar E.Dickey, John W.Swanson, "Colour characterization of Kraft liner Board decker effluent" Paperi Jaa puu, no 4a 1976, 1-9.
2. P.V.R.Subrahmanyan, Sachan P.C., and Mohan Rao G.J. "Aspects of colour removal from Pulp & Paper Mill effluents" Ippta Vol.IX, No.1, 1972.
3. Dubey R.K. & Joshi R.C. "Studies on the removal of colour from pulp mill waste water" Indian Pulp & Paper. April-May, 1980.
4. David C.Eaton, Hou-min Chang, Thomas W.Joyce, Thomas W.Jaffreis and T.Kent Kisk. "Method obtains fungal reduction of the colour of extraction stage kraft bleach effluent" Tappi, June, 1982, Vol.65 No. 6, 89-92.
5. D.Eaton and H-m-Chang, T.K.Kirk "Fungal decolorisation of Kraft bleach plant effluents" Tappi, October 1980, Vol. 63, No. 10, 103-106.
6. T.Kent Kirk and H-m Chang "Potential applications of bioligninolytic system" Enzyme microb technol, 1981, July Vol.3, 189-196.

7. Bist D.P.S., Jangalgi N.R. & Kaul S.S. "Colour reduction of Kraft bleach effluent by the addition of Hypochlorite" Ippta No. XVIII, No.9, Dec. 1980.

8. Bhargava G.G. Dwivedi R.P. Jangalgi, N.R. & Kaul S.S. "An approach to inplant colour reduction of bleach plant effluent using Calcium hypochlorite" Ippta Vol.XVIII, No.3, Sept.1981.

9. Jauhari,M.B. & Maheshwari S. "In plant colour reduction of the bleach effluent " Ippta XI, 3(1974) 196.

10.Kapoor S.K., Pant,R., Roy T.K. and Mathur R.M. "Colour and COD reduction of bleach effluents" Project Ind/73/012

11.J.P.Cassey "Pulp and Paper"2nd ed. Interscience, New York, 1966 pp.483-484.

12.J.H.E.Herbest in "The bleaching of pulp" Monograph No. 27, Tappi, New York, 1963, p. 83.

13.F.Kraft "Pulp & Paper manufacture" 2nd ed. Mc. grewhill, New York 1969, p. 647.

14.Seven A. Rydholm "Pulping Processes" Interscience, New York Fig. 14, 27, p.949.

TABLE - 1

PHYSICO-CHEMICAL CHARACTERISTICS OF GRADE III WASTE WATER

S.No.	Particulars	Flow M3/day	pH	Colour Pt.Co. Unit	BOD_5 mg/l	COD mg/l	S.Solid mg/l	Chloride mg/l
1.	Pulp Mill	-						
	i) Washing & Screening drain	-	9.0-10.5	5000-7000	400-500	1200-2000	600-800	105-140
	ii) Caustic Washing	-	9.0-11.0	4000-8000	400-650	1000-2200	450-600	150-180
	iii) Digester HS Leakages	-	10.5-11.0	5000-8000	300-500	1200-1800	100-250	100-140
2.	Soda Recovery Malone F.Drain	-	10.5-11.5	3000-4000	150-200	400-650	60-150	80-150
3.	Tail end drain							
	No.2 washing & Screening drain of P/Mill Leakages of S/Recy.	5100	10.0-10.5	3500-5000	200-300	1000-1400	200-600	300-550
	No.4 Caustic extraction effluent or pulp mill	11500	10.0-11.5	4000-6000	200-350	1000-1200	150-350	500-650
4.	Grade III inlet to clarifier	16000-17000	6.0-10.0	1590-4850	140-252	484-1035	283-618	320-640

TABLE - 2

DISCOLOURATION OF GRADE III UNTREATED EFFLUENT BY ALUM

S.No.	Alum	pH	Colour Pt.Co. Unit	BOD_5 mg/1	COD mg/1	Chloride mg/1	M-Alkalinity as $CaCO_3$	Settleable solid. g/1
Inlet to Clarifier								
1. Blank	-	7.9	3000	170	992	845	150	-
i)	300	6.0	500	70	592	845	30	0.29
ii)	400	5.7	200	30	552	781	20	0.33
iii)	500	5.5	200	20	558	745	30	0.34
iv)	600	5.4	200	20	504	781	30	0.36
v)	700	5.4	200	40	-	781	40	-
vi)	800	5.4	150	60	-	795	20	-
vii)	900	5.2	100	60	-	795	20	-
Anarobic lagoon outlet								
2. Blank	-	7.6	1650	100	464	646	-	-
i)	600	6.9	500	70	208	604	-	0.186
ii)	650	6.7	350	50	188	600	-	0.186
iii)	700	6.6	750	40	148	589	-	0.275
iv)	750	6.4	100	35	136	589	-	0.277
Polishing Pond Outlet								
3. Blank	-	7.6	850	50	268	703	-	-
i)	600	6.7	500	30	188	682	-	0.150
ii)	650	6.6	300	30	88	675	-	0.100
iii)	700	6.6	150	20	48	675	-	0.092
iv)	750	6.4	100	15	36	667	-	0.090

TABLE -3

DISCOLORISATION OF GRADE-III UNTREATED EFFLUENT WITH ALUM AND POLYELECTROLYTE

S.No.		Alum ppm	PC Powder ppm	True floc S³	pH	Colour Pt.Co. Unit	BOD_5 mg/l	COD mg/l	Chloride mg/l	M-Alkalinity as $CaCO_3$ mg/l	Settleable solids mg/l
1.	Blank	-	-	-	10.1	2000	160	352	270	100	not determined
	i)	200	-	-	8.1	-	-	-	-	180	do
	ii)	300	-	-	7.3	-	-	-	-	90	do
	iii)	400	-	-	6.4	100	160	204	241	50	do
	iv)	500	-	-	5.8	50	120	104	263	30	do
2.	i)	-	200	-	8.4	200	140	252	334	100	do
	ii)	-	300	-	7.5	100	90	245	362	90	do
	iii)	-	400	-	7.0	50	70	240	383	40	do
	iv)	-	500	-	6.9	25	120	220	426	30	do
3.	Blank	-	-	-	7.1	3000	200	1112	646	130	do
	i)	650	-	-	5.0	400	170	504	554	-	do
	ii)	800	-	-	4.9	400	140	520	554	-	do
4.	i)	-	500	-	5.3	250	130	352	731	-	do
	ii)	-	600	-	5.2	200	120	456	724	-	do
5.	i)	100	300	-	5.5	400	130	440	660	-	do
	ii)	200	300	-	5.3	350	110	432	660	-	do
6.	Blank	-	-	-	7.9	1000	200	992	845	150	do
	i)	300	-	10	6.8	600	100	-	739	40	0.04
		400	-	20	6.3	300	50	-	774	30	0.07
		500	-	30	5.7	200	25	-	767	20	0.25
		600	-	40	5.5	100	25	-	748	10	0.32
	ii)	-	-	80)							
		-	-	90)	Flocs do not appear.						
		-	-	100)							

TABLE - 4

DISCOLOURATION OF GRADE III UNTREATED EFFLUENT BY ALUM & FERROUS SULPHATE

S.No.	Alum ppm	$FeSO_4$ ppm	pH	Colour Pt.Co. Unit	BOD_5 mg/l	COD mg/l	Chloride mg/l	M.Alkalinity as $CaCO_3$ g/l	Settleable Solid g/l
1. Blank	-	-	7.1	2000	200	700	568	-	-
i)	500	-	5.5	260	40	272	558	-	0.337
ii)	600	-	5.4	150	25	220	504	-	0.359
iii)	-	800	6.2	-	-	-	-	-	Flocs not formed.
iv)	-	1000	6.0	-	-	-	-	-	do
v)	150	500	5.5	1500	70	672	533	-	0.205
vi)	200	500	5.4	1000	50	560	533	-	0.293
vii)	250	500	5.2	300	30	512	533	-	0.374
viii)	300	500	5.0	200	25	416	533	-	0.473

TABLE -5

DISCOLOURATION OF GRADE III UNTREATED EFFLUENT BY ALUM LIQUID CHLORINE, WASTE LIME AND LIME SLUDGE AS SUCH AS WELL AS SUPERNATENT OF THE LIME SLUDGE

S.No.	Alum dose, ppm	Liquid chlor-ine dose ppm	Waste lime dose ppm	Lime sludge		pH	Colour Pt.Co. Unit	BOD_5 mg/l	COD mg/l	Chloride mg/l	M.Alk. as $CaCO_3$ g/l	Settleable solid g/l
				As such dose g/l	Super-natent mg/l							
1. Blank	-	-	-	-	-	7.9	1000	200	992	845	150	-
i)	-	50	-	-	-	4.9	600	20	432	859	-	0.032
ii)	-	70	-	-	-	4.3	600	30	456	1100	-	0.020
iii)	-	90	-	-	-	3.8	500	80	432	1184	-	0.010
iv)	-	110	-	-	-	3.6	500	70	422	1193	-	0.007
v)	-	150	-	-	-	3.6	300	80	372	1243	-	-
vi)	-	200	-	-	-	3.5	250	70	356	1278	-	-
vii)	-	300	-	-	-	3.4	200	80	336	1335	-	-
viii)	-	500	-	-	-	3.3	100	160	316	V.high	-	-
2. i)	200	50	-	-	-	4.8	500	130	-	866	-	0.038
ii)	300	60	-	-	-	4.4	500	70	-	875	-	0.079
iii)	400	70	-	-	-	4.2	300	50	-	866	-	0.070
iv)	500	80	-	-	-	4.1	250	30	-	875	-	0.016
3. i)	-	100	500	-	-	6.8	600	150	384	966	50	0.02
ii)	-	200	1300	-	-	6.6	500	140	356	1051	40	0.01
iii)	-	300	2000	-	-	5.9	200	70	324	1093	-	-
iv)	-	400	2750	-	-	5.8	100	70	320	1143	-	-

4. i)	-	100	-	0.7	-	7.5	500	180	420	951	70	0.260
ii)	-	200	-	1.17	-	7.5	400	160	408	1185	70	0.894
iii)	-	300	-	1.45	-	7.2	200	90	400	1398	60	0.920
iv)	-	400	-	2.51	-	7.2	100	60	340	1406	60	0.990
5. i)	-	100	-	-	50	6.5	600	100	-	high	40	-
ii)	-	200	-	-	125	5.4	500	80	-	-	-	-
iii)	-	300	-	-	200	5.2	500	70	-	-	-	-
iv)	-	400	-	-	500	5.0	300	60	-	-	-	-

TABLE -6

DISCOLOURATION OF GRADE III UNTREATED EFFLUENT BY CALCIUM HYPOCHLORITE, ALUM, LIQUID CHLORINE & FERROUS SULFATE

S.No.		Ca.Hypo-chlorite ppm	Alum ppm	Liq. Cl_2	$FeSO_4$ ppm	pH	Colour Pt.Co. Unit	BOD_5 mg/l	COD mg/l	Chloride mg/l	M.Alk. mg/l	Settleable solid g/l
A.	<u>Inlet to Clarifier</u>											
1.	Blank	-	-	-	-	9.1	4000	200	888	646	530	-
	i)	100	-	-	-	8.8	2500	160	640	667	620	0.228
	ii)	200	-	-	-	8.2	1200	90	560	845	680	0.231
	iii)	300	-	-	-	8.2	600	60	448	852	710	0.242
2.	i)	100	50	-	-	8.2	1500	140	560	632	520	0.101
	ii)	150	70	-	-	7.5	500	100	480	618	470	0.122
	iii)	200	100	-	-	7.0	200	40	220	611	420	0.150
3.	Blank	-	-	-	-	7.1	2000	200	700	568	535	-
	i)	300	-	-	100	7.0	250	35	224	582	-	0.028
	ii)	300	-	-	200	6.9	250	25	220	511	-	0.156
	iii)	300	-	-	300	6.9	200	15	160	497	-	0.193
	iv)	300	-	-	400	6.9	150	15	128	497	-	0.334
4.	Blank	-	-	-	-	8.0	2000	140	520	696	540	-
	i)	100	-	200	-	6.7	2000	80	424	923	-	-
	ii)	150	-	150	-	7.0	1250	70	440	987	-	-
	iii)	200	-	100	-	7.2	1000	75	504	1037	-	-
	iv)	250	-	50	-	7.5	700	60	480	1086	-	-

B. Aeration Pond outlet

1.	Blank	-	-	-	-	8.0	1650	140	520	696	-	-
	i)	-	-	300	-	6.0	1400	80	488	809	-	0.135
	ii)	100	-	200	-	6.7	1250	80	424	923	-	0.085
	iii)	150	-	150	-	7.0	1000	70	440	987	-	0.075
	iv)	200	-	100	-	7.2	1000	75	504	1037	-	0.080
	v)	250	-	50	-	7.5	850	60	480	1086	-	0.092
	vi)	300	-	-	-	7.7	600	50	384	1157	-	0.118

TABLE -7

ANALYSIS OF GRADE III UNTREATED AND TREATED WASTE WATER

Year/ Month	Flow Untreated m^3/day	Grade III untreated pH	BOD$_5$ mg/l	COD mg/l	S.S. mg/l	Cl. mg/l	Colour Pt.Co. Unit	Flow treated M^3/day	Grade III treated pH	BOD$_5$ mg/l	COD mg/l	S.S. mg/l	Cl. mg/l	Colour Pt.Co. Unit
1985 Octr.	21910	7.9 (6.4-9.8)	210 (120-470)	933 (750-1680)	434 (280-670)	576 (512-675)	-	21460	7.9 (7.9-8.0)	77 (60-90)	649 (612-750)	92 (72-105)	555 (511-596)	-
Novr.	20230	7.4 (5.2-10.4)	292 (150-750)	1000 (544-1360)	361 (140-640)	625 (469-781)	-	14230	7.9 (7.8-8.4)	77 (50-130)	549 (336-768)	85 (40-105)	671 (479-781)	-
Decr.	18910	8.2 (7.0-9.6)	252 (100 400)	1188 (520 4040)	345 (245-560)	528 (284-653)	-	14910	7.9 (7.5-8.4)	72 (25-135)	440 (304-576)	95 (75-130)	675 (440-746)	-
1986 Jany.	19900	8.5 (7.2-10.4)	230 (140-400)	1035 (416-1340)	283 (219-420)	476 (270-639)	-	16900	8.0 (7.8-8.3)	59 (40-80)	488 (350-575)	89 (79-110)	584 (511-724)	-
Feby.	20590	8.5 (7.3-11.3)	234 (140-400)	990 (560-1424)	382 (250-490)	475 (57-653)	-	15860	7.9 (7.7-8.1)	59 (55-60)	496 (392-720)	83 (75-87)	474 (412-611)	-
March	20270	7.4 (7.3-9.4)	194 (100-260)	823 (464-1240)	399 (240-660)	584 (440-660)	2617 (750-4500)	14180	8.1 (8.0-8.4)	58 (50-65)	445 (344-592)	81 (70-92)	576 (426-675)	

April	20590	8.7 (7.2-10.7)	160 (90-330)	658 (432-992)	431 (240-820)	596 (391-824)	2739 (1200-8500)	14730	8.2 (8.0 8.6)	53 (30-80)	327 (178-504)	82 (40-100)	786 (426-923)	1255 (600-2500)
May	16960	9.4 (7.9-10.8)	166 (80-300)	514 (344-1040)	478 (260-824)	724 (447-1037)	2815 (170-9000)	12270	8.3 (8.2-8.6)	46 (35-60)	252 (220-384)	82 (40-161)	912 (682-994)	516 (280-850)
June	20280	9.9 (7.7-11.1)	146 (70-200)	484 (336-1024)	618 (287-1422)	606 (405-817)	2105 (170-9000)	14460	8.2 (7.8-8.9)	38 (35-40)	214 (192-224)	71 (54-89)	870 (618-994)	418 (370-500)
July	21370	9.4 (7.5-11.1)	154 (110-250)	490 (352-1112)	561 (320-974)	617 (355-823)	1598 (370-9000)	19090	8.2 (7.9-8.3)	40 (30-50)	224 (192-264)	81 (67-96)	679 (561-902)	542 (270-720)
August	21910	8.4 (7.7-10.5)	155 (110-200)	494 (360-800)	411 (288-560)	622 (497-852)	2185 (370-4500)	16140	8.3 (7.9-8.8)	41 (30-50)	231 (200-288)	85 (68-98)	695 (604-767)	630 (370-850)