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Synthesis of Nano-Boron and related studies at FCRC

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Background

- FCRC has received a project from GTRE to produce 90 % + pure nano-Boron at ~ 2 kg/month and carry out combustion studies

- But, even before that, due to indications of interest in this product by some segments of DRDO, work had begun at FCRC to understand Boron production process during 2013-2014.

- Using combustion synthesis with Boron trioxide and Magnesium, initial trials produced Boron at a purity that could not be precisely established using the SEM analysis procedure. Values reported from instrument analysis varied between 35 and 85 %. The pathway to good analysis was not easy. What was thought was good was provided for initial testing in LPG flame.

- While I will present the first part on Boron production after the project from GTRE was undertaken. Prof……

…….the boron synthesis procedure

FCRC Boron Synthesis

5 kg
98% Pure

Boric Acid

$\xrightarrow[-H_2O]{\Delta}$

B_2O_3 2.7 kg

Crushing, Grinding & Ball Milling - ~20 hrs

B_2O_3 (40 µm Powder)

Mg 3.375 k g | 40 µm Mg Powder

Heavy Duty Mixing & Ball Milling -Mg with B_2O_3 ~ 8 hrs

6.075 kg Reaction Mixture

Combustion in SS Reactor vessel (~ 250g)~ 4 hrs

5.565 kg

Heavy Duty Grinding ~8 hrs

26.2 kg, 35% HCl

Leaching , Washing ~60 hrs

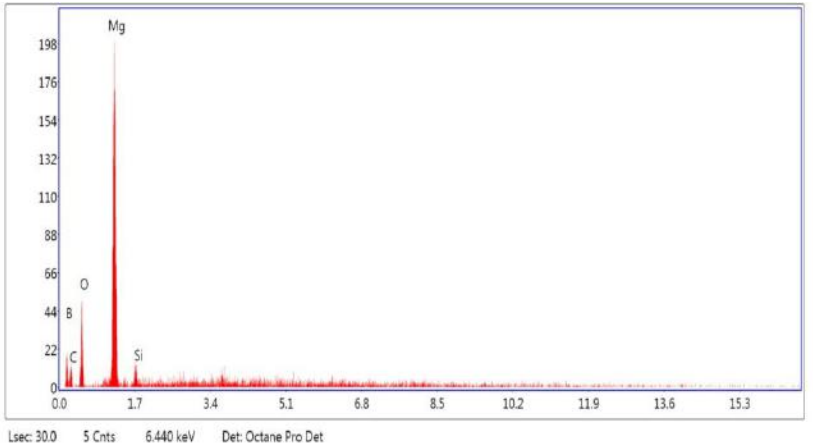
(washing with 70 to 90 L water till $MgCl_2$ goes down to ppm levels)

Vacuum drying & Boron size reduction to <2 µm using high energy ball mill and *special* packing ~8 hrs

~500 g, Boron

Some developmental hurdles

- SEM and EDX analysis were tried out at several labs – CNMS (Jain University), CIIRC (Jyothi Inst. Of technolgy), BMS college, IISc.
- The results from several labs either were indicative or non-confirmative and led to a long winded effort to obtain a reliable analysis procedure.
- However, even with these it was clear that there was significant presence of MgO in undesirable quantities along with Carbon and Silica, calcium and aluminium



- Possible reasons:

Element	Weight %	Atomic %
B	51.68	59.76
C	21.32	22.20
O	15.67	12.24
Mg	10.91	5.61
Si	0.42	0.19

- MgO to incomplete leaching process that could be easily corrected
- But, the entry of carbon particles was thought to have come in during the conversion of Boric acid to Boron trioxide from bio-mass stove and Silica to input material quality and other elements also similarly from raw material

- This needed revisiting the process and effect minor changes to improve the final product quality

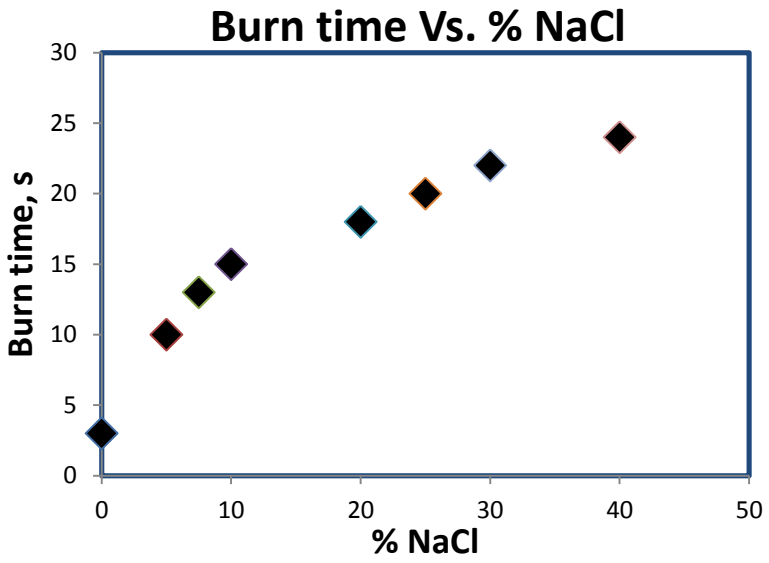
How these issues are addressed?

- Changes made to the existing process:

  - Process started directly from high quality B_2O_3 procured from market. It turns out that this is also cheaper.
  - Based on an input from the intermediate GTRE review process, it was decided to examine the use of Sodium chloride (LR grade) at various fractions from the point of view of controlling the exothermicity (see next slide). It was also supposed to improve the product quality in getting to nano-sizes according to *Yujing Ou etal (2015)*.
  - Based on the experiments, NaCl fraction was introduced at 35%.
  - Thus the initial combustion mixture had B_2O_3:Mg:NaCl used at 1:1.05:0.71 (w)
  - Using Heavy duty mixer grinder to prepare the initial composition to ensure fine particle size during the combustion reaction.
  - Nitrogen atmosphere blanket was used for ensuring inert environment.
  - Leaching was carried out in HCl/ NaOH/ HF sequence to remove minor compounds *(Zhou etal 2015)*
  - *A* study on temperature during leaching by 14% HCl is also carried so as to check if the temperature reaches boiling leading to loss of Boron during leaching

Studies with NaCl

S. No	NaCl	Mass burnt	Duration	Burn rate
	%	g	s	g/s
1	0	20	3	6.67
2	5	20	10	2.00
3	7.5	20	13	1.54
4	10	20	15	1.33
5	20	20	18	1.11
6	25	20	20	1.00
7	30	20	22	0.91
8	40	20	24	0.83
9	50	did not burn		

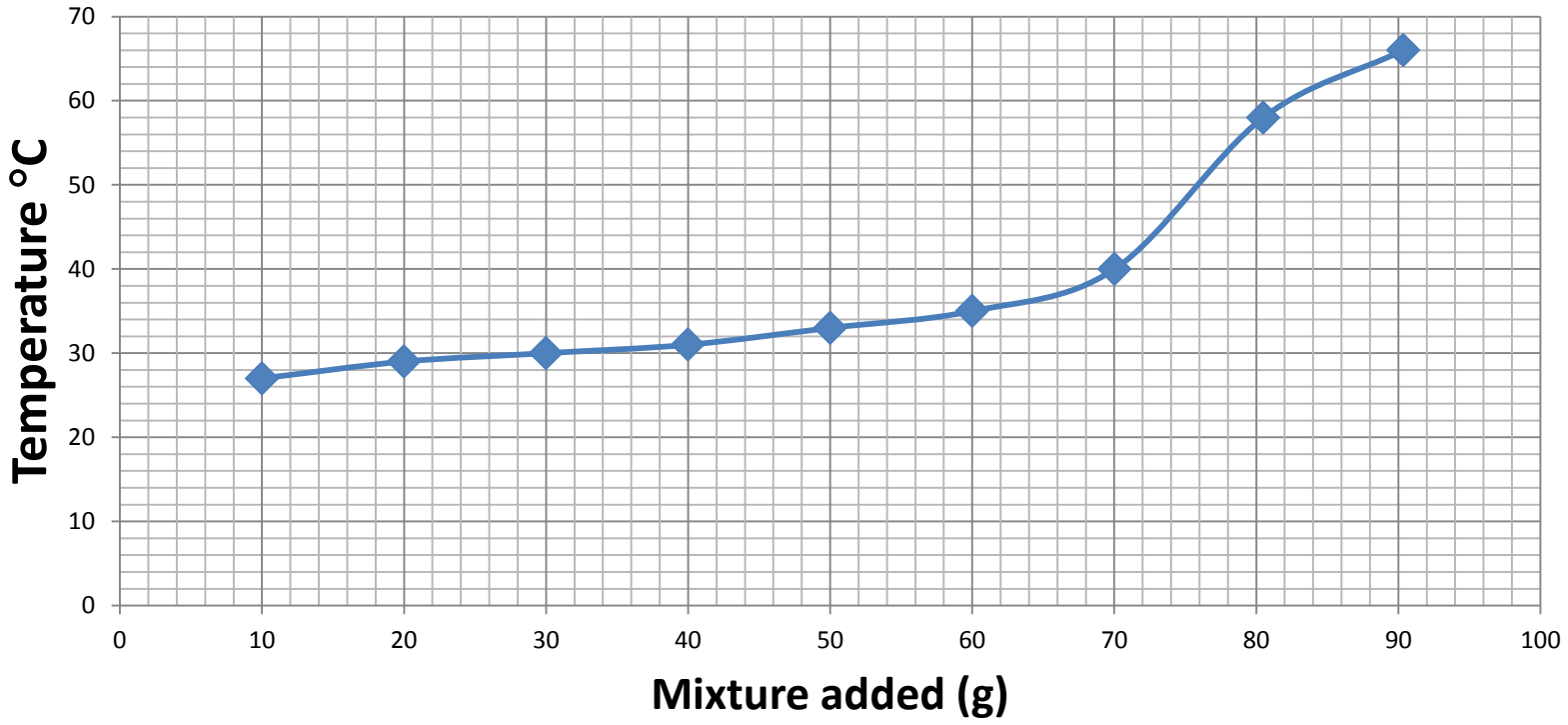


- $B_2O_3 + 3Mg + x\ NaCl = 2B + 3\ MgO + x\ NaCl$

- Studies conducted with varying % NaCl (w) addition to stoichiometric reaction mixture indicated 35% NaCl addition is beneficial as the reaction temperature do not exceed 1000 °C (thermocouple measurement)

Reaction temperature during leaching

About 90 g of ignited mixture is added to 800 ml of 14% HCl @ 10 g / 5 minutes and temperature is recorded with constant stirring using a magnetic stirrer. Maximum temperature reached is **66 °C and ΔT 39 °C.** Thus, possible escape of boron during the leaching process is avoided.



Issues related to SEM & EDX

- Two identical samples prepared using the improvised process are tested in different labs
- Results indicate that a poorer SEM & EDX equipment produces a mistaken signature of Mg for B and in an unrealistic manner

Composition	CENSe	BMSCE
	Wt%	Wt%
Boron	92.87	56.69
Magnesium Oxide	1.04	28.23
Aluminium Oxide	0.42	0
Silica	1.14	0.87
Others	4.53	14.21

Improvised FCRC Synthesis Improvised

B_2O_3 : Mg : NaCl
1:1.05:0.71 (w)

Reaction Mixture (~4.9 kg)

Heavy Duty Mixing & grinding (~ **4 hrs**)

Combustion in SS Reactor vessel with Nitrogen gas purging (batch size ~ 250g)~ **4 hrs**

~ 4.4 kg ignited mixture

Heavy Duty Grinding **~2 hrs**

~ 4.3 kg fine ignited mixture

Washing, Leaching , Washing by recirculation & centrifugation
~**46 hrs** **(washing with HCl / NaOH/ HF / water)**

Vacuum drying & Boron size reduction to <2 µm and special packing ~**8 hrs** **(500 g Boron)**

Chemical requirements

Estimated quantity of raw materials for preparing 1 kg of Boron

S.No	Chemical Name	Quantity	Cost Rs.
1	Boron trioxide, kg	3.7	919.00
2	Magnesium, kg	3.8	3780.00
3	Sodium chloride, kg	2.4	242.00
4	35% HCl, litres	25	4977.00
5	NaOH pellets LR grade, kg	0.63	252.00
6	40% HF, litres	0.91	197.00
7	DM water 20L bottle	4	225.00
8	Ethanol	0.1	52.00
	Total		10644.00

Note: Thus the cost of raw materials is Rs. 11/g.

If the large scale production is planned, one can expect the cost of production governed by the raw materials should be way below the current costs from overseas – China including.

Final Product Quality and Result Comparison

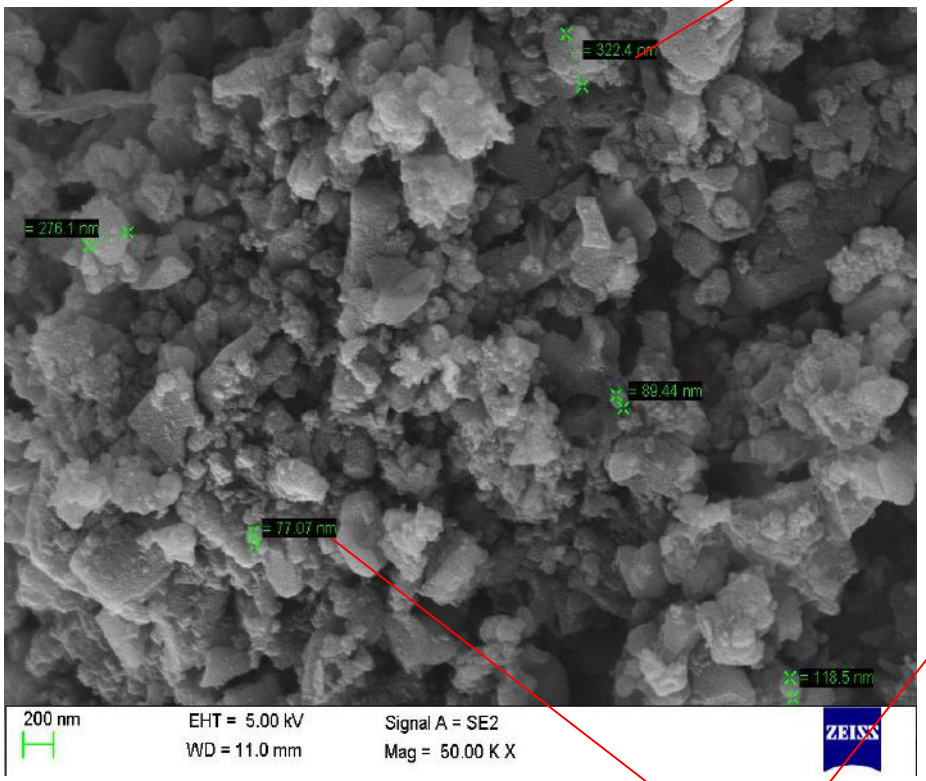
Composition by mass	FCRC Final Sample	GTRE	Ref: MERCK	FCRC Earlier Sample
Boron %	92.87	80.67	99.39	71.48
MgO %	1.04	12.0	0.20	13.7
SiO_2 %	1.14	4.15	0.00	2.87
Al_2O_3%	0.42	0.81	0.00	0.43
Others %	4.53	2.37	0.41	11.52
Total %	100.00	100.00	100.00	100.00

Note: FCRC sample 1&2 are prepared with NaCl addition at 35% to stoichiometric mixture of B_2O_3 and Mg and. Final sample is Boron synthesised from Purchased B_2O_3; Earlier sample: Boron synthesised from B_2O_3 produced at FCRC.; Boron from GTRE is indicated as Grade 2

SEM Results

FCRC PRODUCT

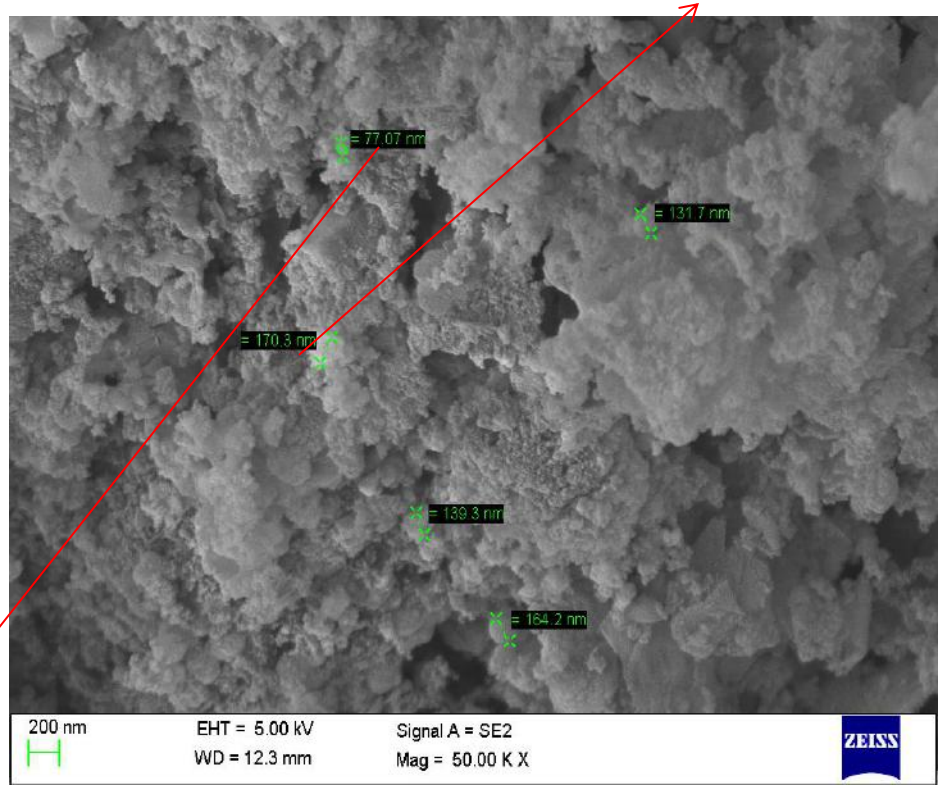
322 nm



77 nm

GTRE SAMPLE

170 nm



Note: Samples Analysed at CENSE, IISc: FCRC sample in the range of 77nm to 322 nm Mean being 251 nm. The GTRE sample may have agglomerated because of possible exposure to atmosphere

Particle size distribution

Analysed at CENSE, IISc

Results indicate effective diameter of 251 nm

Brookhaven Instruments Corp.
ZetaPALS Particle Sizing Software Ver. 5.23

Date: Jan 22, 2019
Time: 11:18:09
Batch: 1901

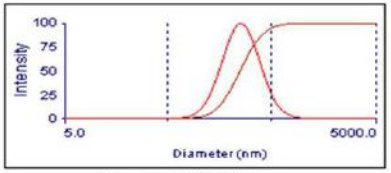
Sample ID	**SAMPLE 1 (Combined)**
Operator ID	**Unknown Operator**
Notes	**BATCH NO. 190104**

Measurement Parameters:

Temperature	= 25.0 deg. C	Runs Completed	= 5
Liquid	= Water	Run Duration	= 00:00:30
Viscosity	= 0.890 cP	Total Elapsed Time	= 00:02:30
Ref.Index Fluid	= 1.330	Average Count Rate	= 359.8 kcps
Angle	= 90.00	Ref.Index Real	= 1.450
Wavelength	= 658.0 nm	Ref.Index Imag	= 0.000
Baseline	= Auto (Slope Analysis)	Dust Filter Setting	= 30.00

SAMPLE 1 (Combined)

Effective Diameter: **251.1 nm**
Polydispersity: **0.184**
Baseline Index: **9.1/ 97.88%**
Elapsed Time: **00:02:30**



Lognormal Distribution

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	230.3	92.0	0.160	8.9/100.00%
2	254.3	101.3	0.159	5.9/ 98.23%
3	257.3	128.5	0.250	9.6/100.00%
4	246.9	123.2	0.249	8.1/ 91.23%
5	266.7	109.2	0.168	6.6/100.00%
Mean	251.1	110.9	0.197	7.8/ 97.89%
Std. Error	6.1	6.7	0.021	0.7/ 1.70
Combined	251.1	107.6	0.184	9.1/ 97.88%

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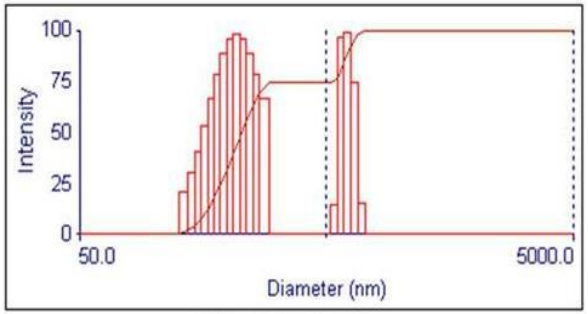
Date: Jan 22, 2019
Time: 11:18:09
Batch: 1901

Sample ID	**SAMPLE 1 (Combined)**
Operator ID	**Unknown Operator**
Notes	**BATCH NO. 190104**

Elapsed Time	00:02:30
Mean Diam.	306.6 nm
Rel. Var.	0.332
Skew	1.084



Multimodal Size Distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
98.6	0	0	203.5	96	39	434.1	0	75
105.5	0	0	216.1	99	48	464.4	0	75
112.8	0	0	229.6	96	56	496.7	0	75
120.7	0	0	243.9	89	63	531.4	14	76
133.3	21	2	259.0	79	70	568.4	97	84
141.6	30	4	275.2	67	75	608.0	100	93
150.5	41	8	310.0	0	75	650.4	74	99
159.8	53	12	331.6	0	75	695.7	15	100
169.8	67	18	354.7	0	75	744.2	0	100
180.3	79	24	379.4	0	75	796.1	0	100
191.5	89	31	405.8	0	75	851.6	0	100

Specs vs. Quality achieved

- The purity of Boron obtained through the improvised process is ~93% with effective diameter 251 nm. Also SEM results indicate particle sizes in the range of 77 nm to 322 nm

- These quality results indicate that the required parameters of >90% purity and particle size range of 0.5 micron to 2 microns as per the project goals are achieved

Summary

- Boron with required purity of >90% and particle size with effective diameter of 250 nm is produced with the improvised process

- The cost of the boron so produced has material cost component of Rs. 11 per g. Expected cost of production at reasonable scale of hundreds of kg/year must be reasonable (perhaps around Rs. 50 per g compared to Rs. 600 per g from overseas)

- Limited study of introducing this into kerosene shows significant agglomeration.

- Attempts are also being made to coat the Boron with fluropolymers so as to improve the fluidisation and prevention of possible surface oxidation to the minimum

References

- Yujing Ou, Peiqing La, Dandan Zhu, and Yalong Zhu, Preparation and Characterization of Amorphous B Powders by Salt-Assisted SHS Technique, Hindawi Publishing Corporation Advances in Materials Science and Engineering Volume 2015, Article ID 287143, 7 pages,http://dx.doi.org/10.1155/2015/287143
- Jiaojiao Zhou and Peng Bai, A review on the methods of preparation of elemental boron, Asia-Pac. J. Chem. Eng. 2015; 10: 325–338 DOI: 10.1002/apj.1892


Thank you!