How Ph.D. Students Start a Research

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

Short Communication

ABSTRACT

In education pedagogy, its necessary to prioritize tasks and jobs. Learn operating the reactor or required apparatus but most important first. Regarding measuring techniques (PSD measurement, pH measurement, XRD, SEM/EDS), learn more basic and fundamental techniques first followed by complimentary techniques. Regarding mineral carbonation, operation of reactor is a basic need followed by particle size measurement using Malvern Mastersizer and powders samples XRD analysis and identifying the phases and verifying those phases through TGA analysis. This article illustrates author personal research of 4 initial 4 months duration. Month wise progress is presented in this article in an interesting way.

1. INTRODUCTION

Reduction in greenhouse gases deemed necessary as their concentration rise sharply from 280 ppm to 419 ppm (1975-2021). Mineral carbonation [1-14], geological storage, oceanic storage and biomineralization as well as chemicals production especially fuels are basic technologies in use. Mineral carbonation is a

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permanent fixation of CO_2. A case report of the 4 months research startup which can be considered as author note is demonstrated here. Data and graphs may have been rough but illustrate the future direction of research progress.

2. MATERIALS, METHODS AND EXPERIMENTAL SET-UP

Materials, Methods and experimental set-up is already discussed and shown in earlier publications [1,9,12,13,15,16].

3. RESULTS AND DISCUSSION

Results and discussions are presented in this section. Month wise activities are presented for Month 1, Month 2, Month 3 and Month 4.

3.1 Month 1 Activities

3.1.1 Weekly report

Summary of weekly activities: The main activities done in the last week are described below:

1. Prepared the 15% and 20% dunite slurry by wet grinding in the ball mill for reactor operation
2. Completed online XRD training for qualitative XRD analysis and obtained booking for induction/training/sample analysis
3. Studied quantitative XRD analysis methods and especially fitting full diffraction patterns method which looks more suitable for quantitative calculations.

The main activities planned for next week are:

1. To run the reactor for 15 wt%, 20 wt% and 25 wt% Dunite slurry
2. Do the in-situ pH measurements and analyse to check whether $NaHCO_3$ is consumed in the reaction or not
3. Dry the slurry for XRD analysis

Summary of weekly activities for next weeks: The main activities done in the last week are described below:

4. Performed the carbonation reaction for 15 wt% dunite slurry at 600 rpm, 130 Bar and 185 °C for 1 h

5. Perform three pH measurements, when experiment started, it was 10, dropped to 8.3 after 30 minutes and to 8.0 after 60 minutes, indicating a minor amount of $NaHCO_3$ is consumed
6. PSD by Malvern Mastersizer (Tests were conducted twice and average taken)

The main activities planned for next week are:

1. To run TGA to calculate the conversion for the reaction
2. Perform XRD analysis of the feed material and reaction product to check which phases are present, it will also provide information that whether feed material have $CaCO_3$ or $FeCO_3$ and will further clarify either lizardite react or not
3. Perform ICP-OES analysis of the supernatant solution after the reaction, it will provide information about concentration of magnesium or calcium and other minerals (including silicon) which have not reacted and yield the solid phase.

3.2 Requirements

1. May we can get some more olivine rich material, because Lizardite (60%, as per optical microscopy) in this Dunite will not react without heat treatment, so yield is expected to be low. Later published research indicated this fact [1, 15].
2. To measure amorphous silica, Reitveld Refinement method will not work, because silica does not yield any peaks in XRD. The suitable method for this is fitting full diffraction pattern using FULLPAT. But we need pure individual minerals (few gram) for this method. Pure olivine, lizardite, magnesite ($MgCO_3$), siderite, brucite, clinopyroxene, amorphous silica, magnetite (Fe_3O_4) etc are present as phases in XRD analysis. Corundum or silicon demanded.
3. To measure only lizardite, corundum reference material is required for quantitative XRD (using intensities comparison method). Our research group and especially my published research used silicon as a reference material [1, 9, 12, 13, 15, 16].

3.3 Month 2 Activities

3.3.1 Weekly reports (4 reports)

Summary of weekly activities: Grinded, 1.1 kg Dunite several times in roller ball mill and got two fractions of fine material, PSD analysis by Malvern Mastersizer report, 30 μm average size.

Operated TGA for reactor product from 25 ^{0}C to 800 ^{0}C @ 10 ^{0}C/min. Two mass losses were observed, the later looks due to the $CaCO_3$ decomposition. Initially a gradual mass increase was observed. Which can be attributed to water mass loss or bit later to brucite decomposition material [1, 9, 12, 13, 15, 16].

3.3.2 Summary of weekly activities

1. Regrind the sub 100 μm material in a ball mill for two hours and perform PSD analysis.
2. Operate the reactor at 128 Bar and 185 ^{0}C for 60 min and samples after 15 min were taken. Then slurry was removed, solids separated and regrinding was done for 20 min in ball mill (MTI Corporation, USA) using twenty five balls of each three smallest sizes. Then again reaction was done at 128 Bar and 185 ^{0}C for 30 min and samples were taken. This is a regrinding after the first phases of reaction, published results can be seen here [15]. Pressure variations were observed.

3.3.3 Summary of weekly activities

I made few important observations which are not seen in the literature till date (October 2014).

Decrease in particle size was observed during the reaction in initial hour because of particles dissolution, but no increase in particle size at end of reaction. When I regrind the material after 60 min, particle size decreased and I again performed the carbonation reaction for 30 min. This time at end of experiment, an increase in particle size was observed. I postulate (can be verified by SEM) that after the first reaction, the magnesite formed has acted as seed particles for the next 30 min reaction, that's why there is increase in size after the reaction. I expect that relatively yield will be higher in the reaction from 60-90 min because of inherent magnesite seeding (related research is here [17]. I expect that if we run the reaction after regrinding for

long time, Yield/conversion will further increase rapidly. Hence, yield can also be increased more with seeding initial first hour reaction. One other important observation is that increase in particle size was more for 20 wt % solids slurry than 15 wt% solids slurry suggesting more yield for 20 wt% solids slurry.

Test 2 conditions, 15 wt% solids, 0.64 M $NaHCO_3$, 128 Bar and 185 ^{0}C for 60 min and samples after 15 min were taken. Then slurry was removed, solids separated by gravity setting and regrinding was done for 20 min in ball mill using twenty five balls of each three smallest sizes. Then again reaction was done at 128 Bar and 185 ^{0}C for 30 min and samples were taken after 15 min. Published and improved results can be seen here [1].

Test 3 (20 wt% solids, 0.64 M $NaHCO_3$, 128 Bar and 185 ^{0}C). Operated reactor for 60 min and samples after 15 min were taken. Before taking the sample, Syringe Pump was started and reactor was slightly pressurized. After 60 min, reaction was stopped and slurry removed, solids separated, and regrinding was performed for 20 min in ball mill using twenty five balls of each three smallest sizes. Then again reaction was perfomed at 128 bar and 185 ^{0}C for 30 min and samples were taken after 15 min and before taking the sample reactor was slightly pressurized with Syringe Pump. Samples for particle size distribution were taken by stirring the slurry before sampling. Soon later, Syringe Pump was replaced with CO_2 booster compressor, both results were matching as working pressure was same.

3.4 Month 4 Activities

3.4.1 Weekly reports

Summary of weekly acgtivities: I Run TGA many times with Calcium oxalate hydrate (99 % pure) to calibrate it.

Resluts are shown in Table 8.

1. Done ICP-OES analysis for test 2 (15 wt% solids, 185 °C, 128 bar) supernatant to measure concentartion of different metals.
2. Done ICP-OES analysis for test 3 supernatant.

Month 4 of Research Start-Up: Activities performed are listed below.

3.4.2 Weekly reports

1. Material was analysed by XRD technique
2. Feed material was analysed to identify the phases present. Test 2 (15 wt % solids slurry carbonated after 60 min) before regrinding and after regrinding was analysed. Test 2 carbonated product top and bottom surface layer was analysed separately.

Table 1. PSD analysis

Test No	Particle Size Distribution before			Particle Size Distribution after		
	D_{90}	D_{50}	D_{10}	D_{90}	D_{50}	D_{10}
	µm	µm	µm	µm	µm	µm
	34.82	7.96	1.64	30.4	10.11	1.75

Table 2. PSD analysis

Result Units	Volume diameters (average particle size, d_{10}, d_{50}, d_{90})
Dx (10)	5.08 µm
Dx (50)	29.1 µm
Dx (90)	70.0 µm
Dx (10)	2.25 µm
Dx (50)	20.5 µm
Dx (90)	73.4 µm

Table 3. PSD analysis

Dunite slurry (15 wt % solids) at 600 rpm	Time (min)	Temperature ^0C	Pressure Bar	pH
	0	185	128	9.0
	10	185	128	
	20	185	124	15 min 7.7
	30	185	120	8.0
	40	185	128	45 min 8.0
	50	185	124	
	60	185	123	8.20
	Regrinding 20 min			
	0	185	128	
	70	185	126	
	80	185	121	75 min 7.8
	90	185	120	8.0

This may be raw data, but is shown as observed. Later experiments may have improved the results

Table 4. PSD analysis

	Particle Size Distribution		
	D_{90}	D_{50}	D_{10}
	µm	µm	µm
Initial feed	54	16	2.4
After 60 min reaction, Before regrinding	49	11	3.3
After regrinding	24.5	6.7	2.3
End of experiment, after 90 min reaction	31.5	8.8	3

Table 5. Test 2, Test repeated for particle size distribution

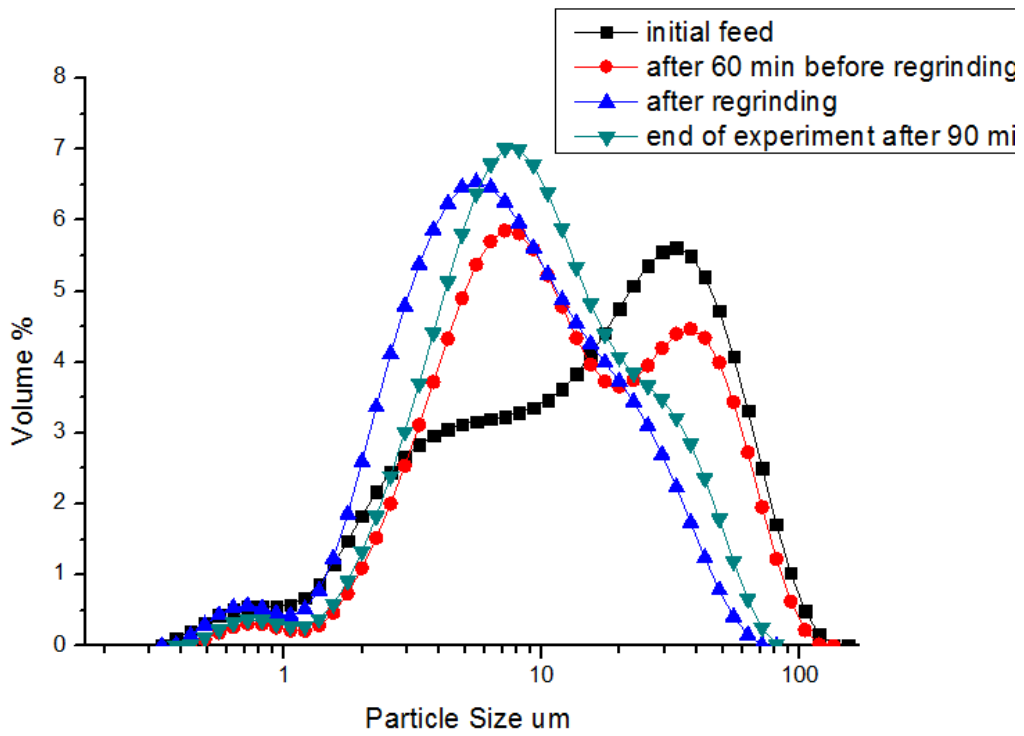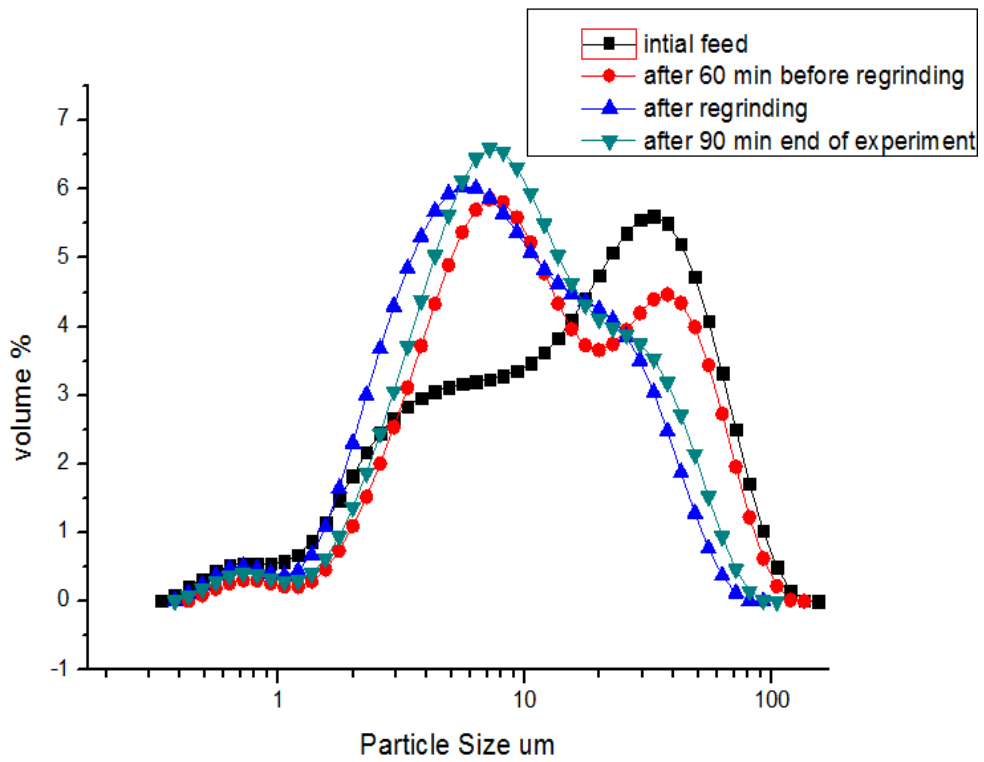|	Particle Size Distribution		
	D_{90}	D_{50}	D_{10}
	um	um	um
Initial feed	54	16	2.4
After 60 min reaction, Before regrinding	49	11	3.3
After regrinding	28.8	7.65	2.41
End of experiment after 90 min reaction	34.2	9.06	2.96

Fig. 1. PSD analysis

Fig. 2. PSD analysis

Table 6. Reactor operating conditions and pH analysis

Dunite slurry (20 wt % solids) at 600 rpm	Time (min)	Temperature ^{0}C	Pressure Bar	pH
	0	185	128	9
	10	186	127	
	20	185	128	15 min 8.00
	30	185	127	8.00
	40	185	127	45 min 7.7
	50	185	127	
	60	185	127	8.2
	Regrinding 20 min			
	0	183	126	
	70	185	125	
	80	185	126	75 min 7.6
	90	185	124	8.00

pH was almost constant during the experiment. Slight variation is due to pressure fluctuation while sampling and pressurizing before sampling. Hence, NaHCO$_3$ was not consumed in the reaction

Table 7. Particle size distribution Test 3

	Particle Size Distribution		
	D_{90} μm	D_{50} μm	D_{10} μm
Initial feed	54	16	2.4
After 60 min reaction, Before regrinding	44.1	10.2	3.22
After regrinding	37.4	8.8	2.8
End of experiment after 90 min reaction	52.4	12.6	3.26

Table 8. TGA calibration

Step	Reaction	Theoretical Mass loss %	Measured Loss Test 1 15 ^{0}C /min %	Measured Loss Test 2 5 ^{0}C /min %	Measured Loss Test 3 10 ^{0}C /min %
1	$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$	12.33	10.785	11.73	10.2
2	$CaC_2O_4 \rightarrow CaCO_3 + CO$	19.17	18.3	18.7	18.8
3	$CaCO_3 \rightarrow CaO + CO_2$	30.12	31.4	30.3	31.3
	Literature Peak temperature with 10 ^{0}C/min	161 478 744	180 490 720	161 472 698	180 495 735

Table 9. Matched Phases

Ref. Code	Compound Name	Chemical Formula	Chemical Name
96-900-0167	Forsterite	Mg7.20 Fe0.80 Si4.00 O16.00	
96-900-6398	Olivine	Co1.00 Mg7.00 Si4.00 O16.00	
96-900-1639	Lizardite	Si2.00 Mg3.00 O9.00 H4.00	
96-100-0055	Brucite	Mg1.00 O2.00 H2.00	
96-900-2325	Magnetite	Fe24.00 O32.00	

Table 10. Matched phases

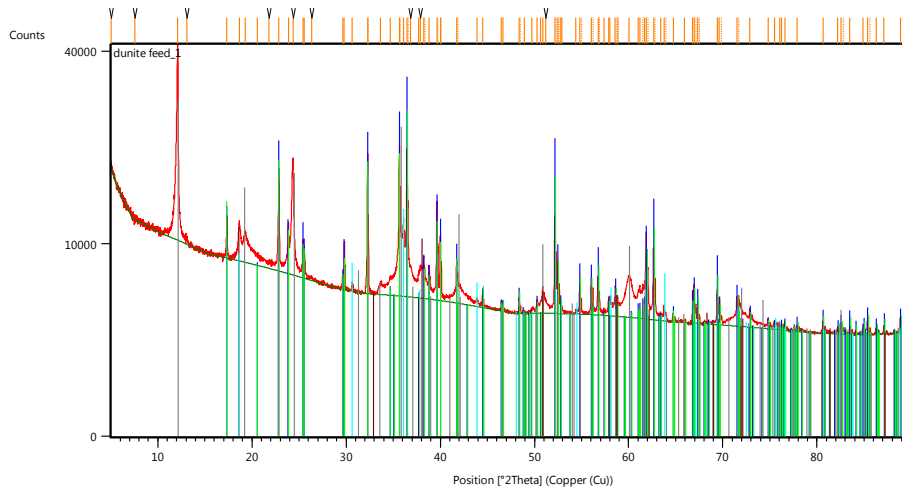| Ref. Code	Compound Name	Chemical Formula	Chemical Name	Mineral Name
96-900-5920	Olivine	Mg7.27 Fe0.66 Ni0.04 Mn0.01 Ca0.03 Si4.00 O16.00		Olivine
96-900-0974	Magnesite	Mg6.00 C6.00 O18.00		Magnesite
96-900-2324	Magnetite	Fe24.00 O32.00		Magnetite
96-900-4510	Lizardite-1T	Mg3.00 Si2.00 O9.00		Lizardite-1T
96-900-5435	Clinopyroxene	Na2.00 Ca2.00 Fe4.00 Si8.00 O24.00		Clinopyroxene

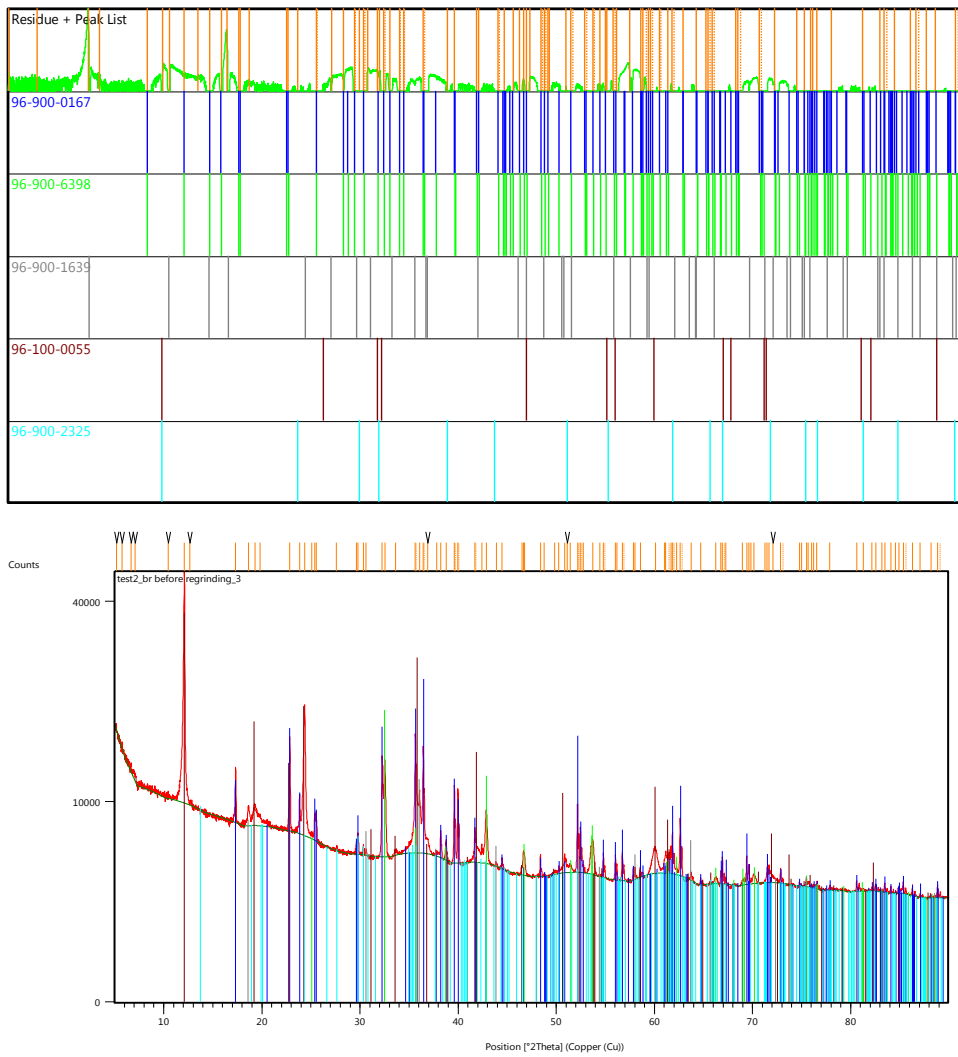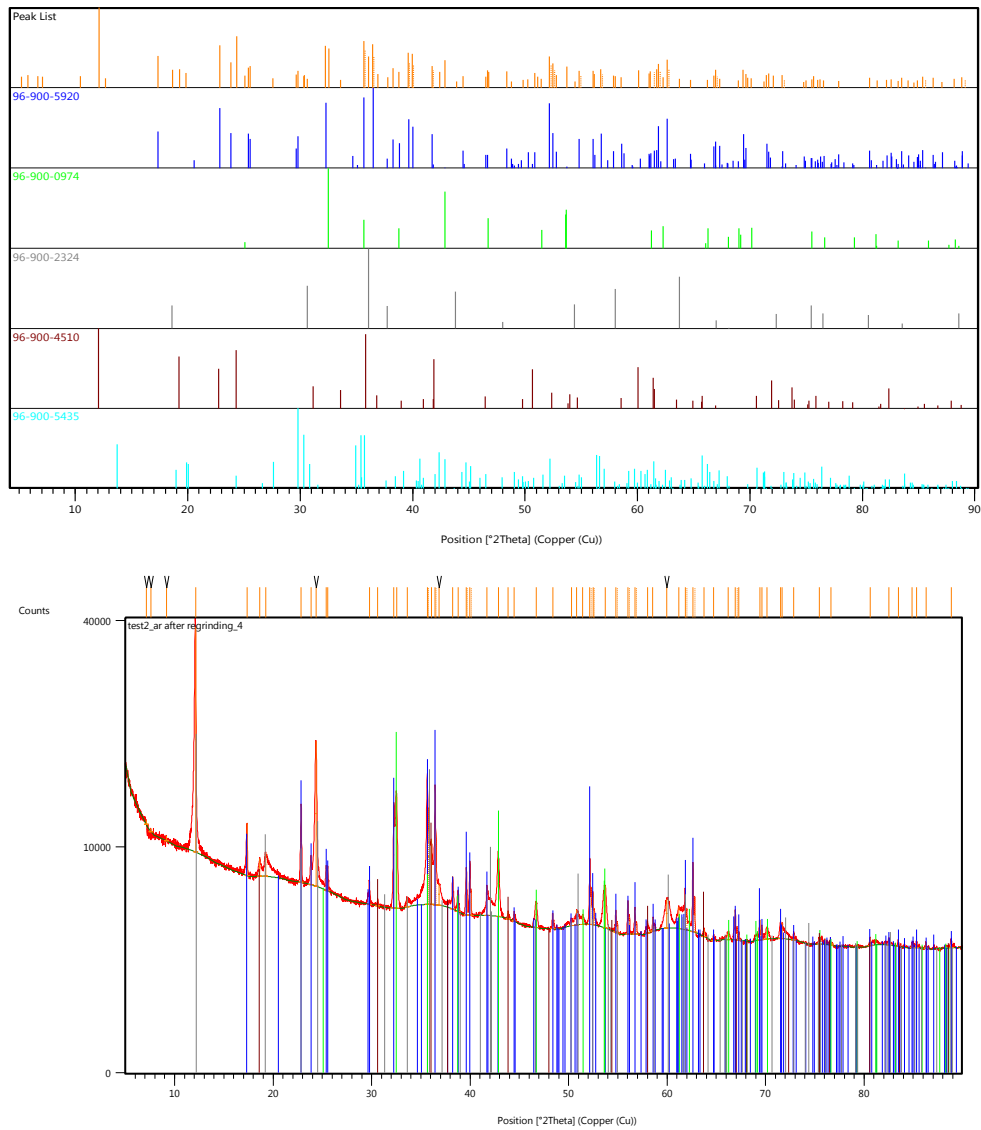**Fig. 3. Feed material**

Fig. 4. Test 2 before regrinding

Fig. 5. Test 2 after regrinding

Table 11. Matched phases

Ref. Code	Compound Name	Chemical Formula	Chemical Name	Mineral Name
96-900-5857	Olivine	Fe0.76 Mg7.24 Si4.00 O16.00		Olivine
96-900-0974	Magnesite	Mg6.00 C6.00 O18.00		Magnesite
96-900-1779	Lizardite-1T	Si2.00 Mg3.00 H6.00 O9.00		Lizardite-1T
96-900-2324	Magnetite	Fe24.00 O32.00		Magnetite

Table 12. Matched phases

Ref. Code	Compound Name	Chemical Formula	Chemical Name	Mineral Name
96-900-5857	Olivine	Fe0.76 Mg7.24 Si4.00 O16.00		Olivine
96-900-0973	Magnesite	Mg6.00 C6.00 O18.00		Magnesite
96-900-1779	Lizardite-1T	Si2.00 Mg3.00 H6.00 O9.00		Lizardite-1T
96-900-2324	Magnetite	Fe24.00 O32.00		Magnetite
96-900-6777	Periclase	Mg4.00 O4.00		Periclase
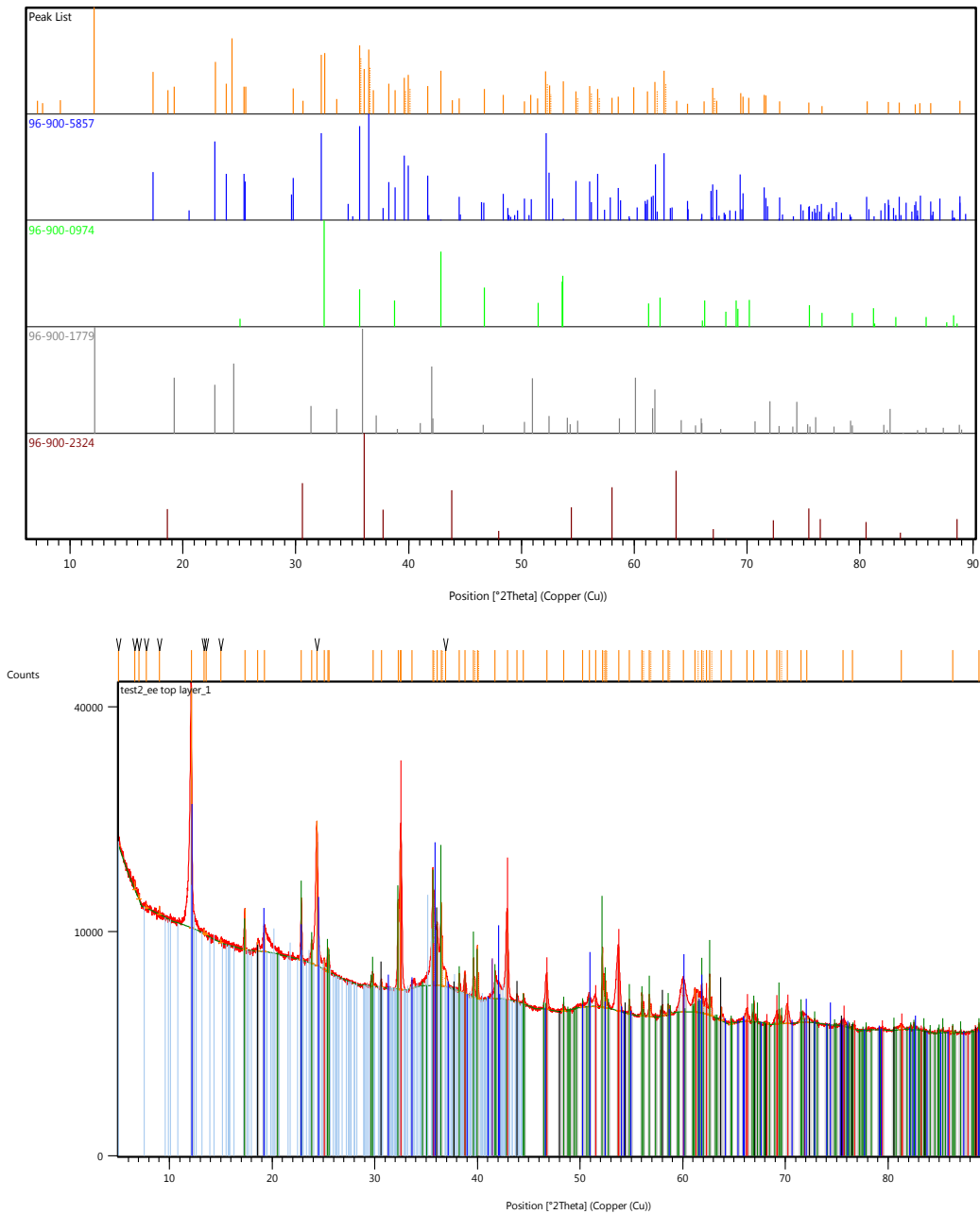
Fig. 6. Test 2 top layer

Table 13. Matched phases

| Ref. Code	Compound Name	Chemical Formula	Chemical Name	Mineral Name
96-900-5857	Olivine	Fe0.76 Mg7.24 Si4.00 O16.00		Olivine
96-900-0974	Magnesite	Mg6.00 C6.00 O18.00		Magnesite
96-900-4509	Lizardite-1T	Mg3.00 Si2.00 H4.00 O9.00		Lizardite-1T
96-900-2324	Magnetite	Fe24.00 O32.00		Magnetite
96-900-6475	Periclase	Mg4.00 O4.00		Periclase
96-900-3800	Magnesioferrite	Mg8.00 Fe16.00 O32.00		Magnesioferrite
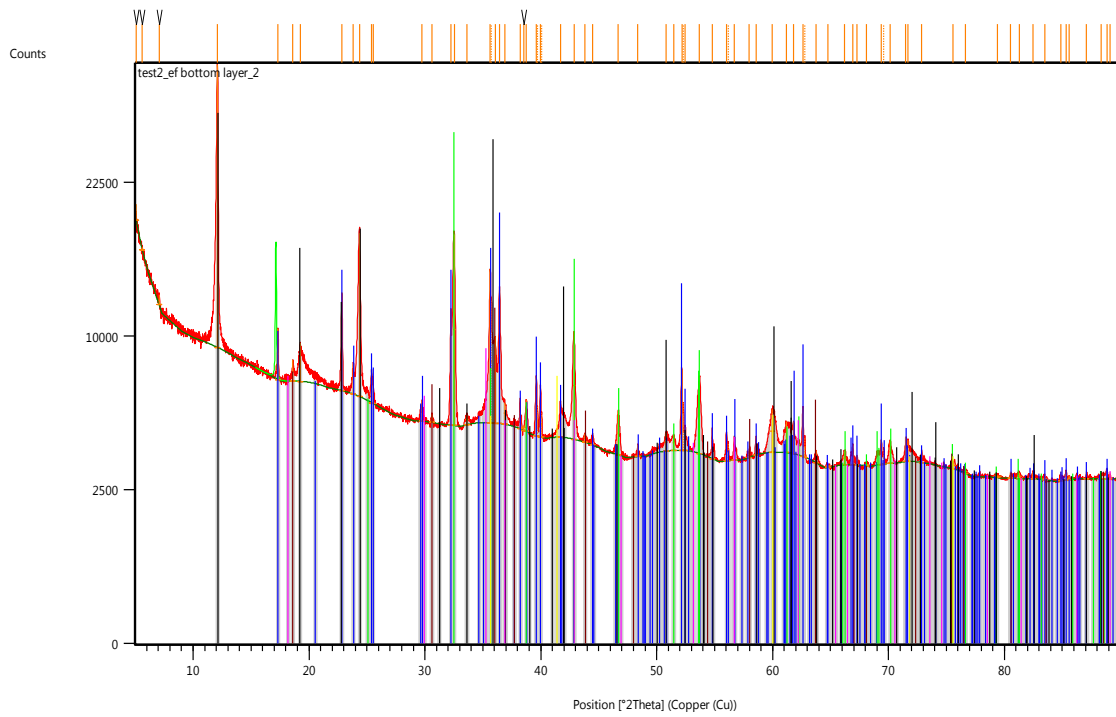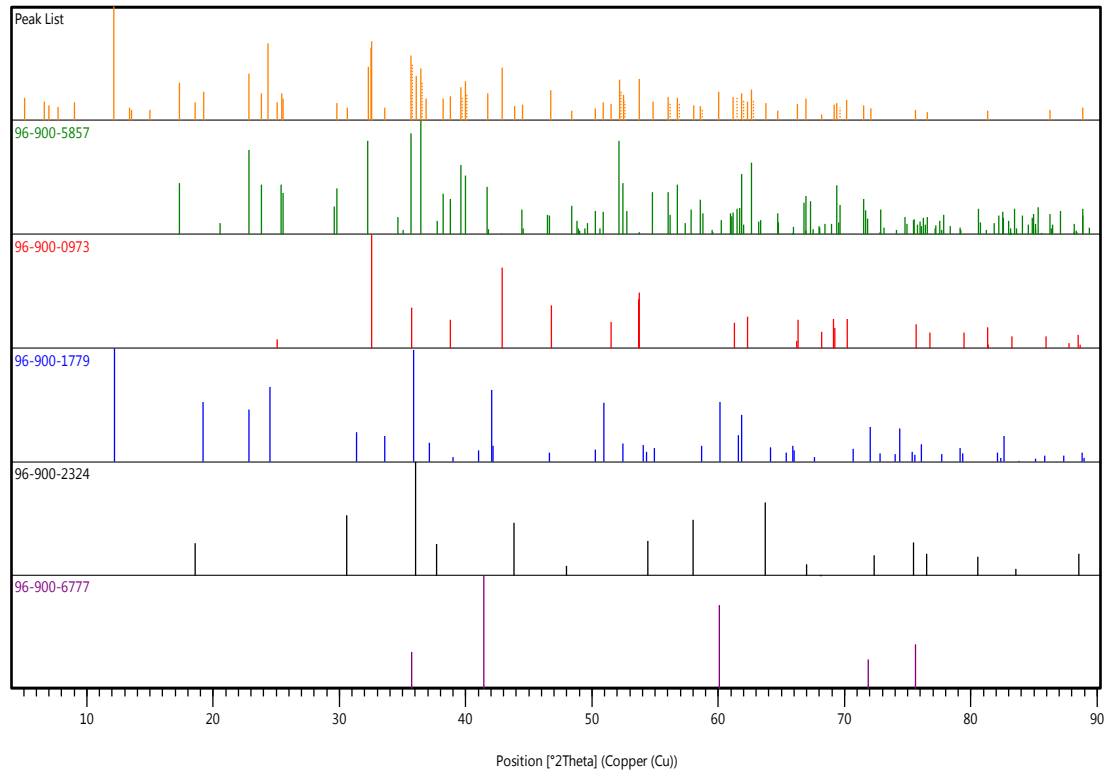
Fig. 7. Test 2 bottom layer
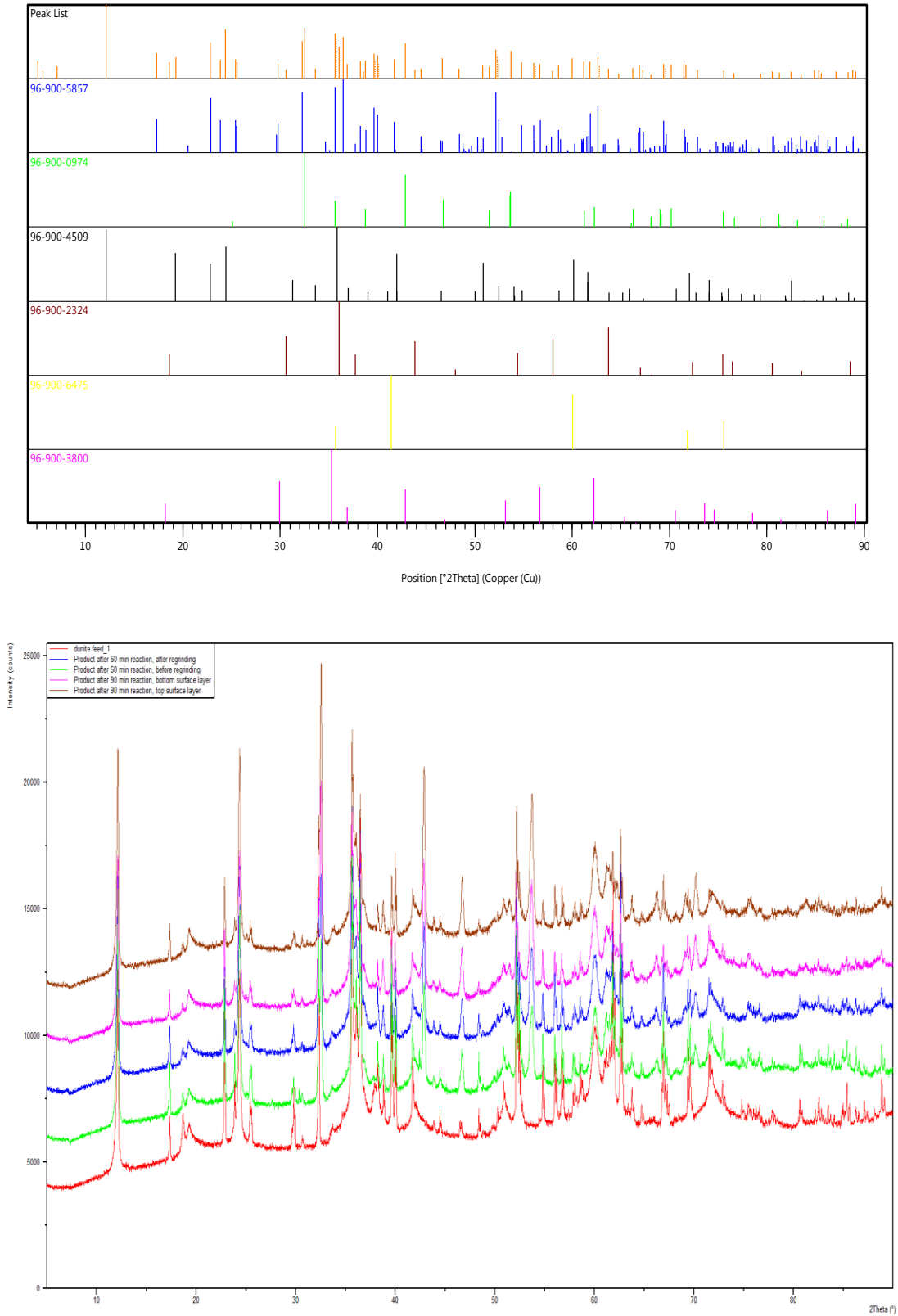
Fig. 8. Summed pattern for XRD results
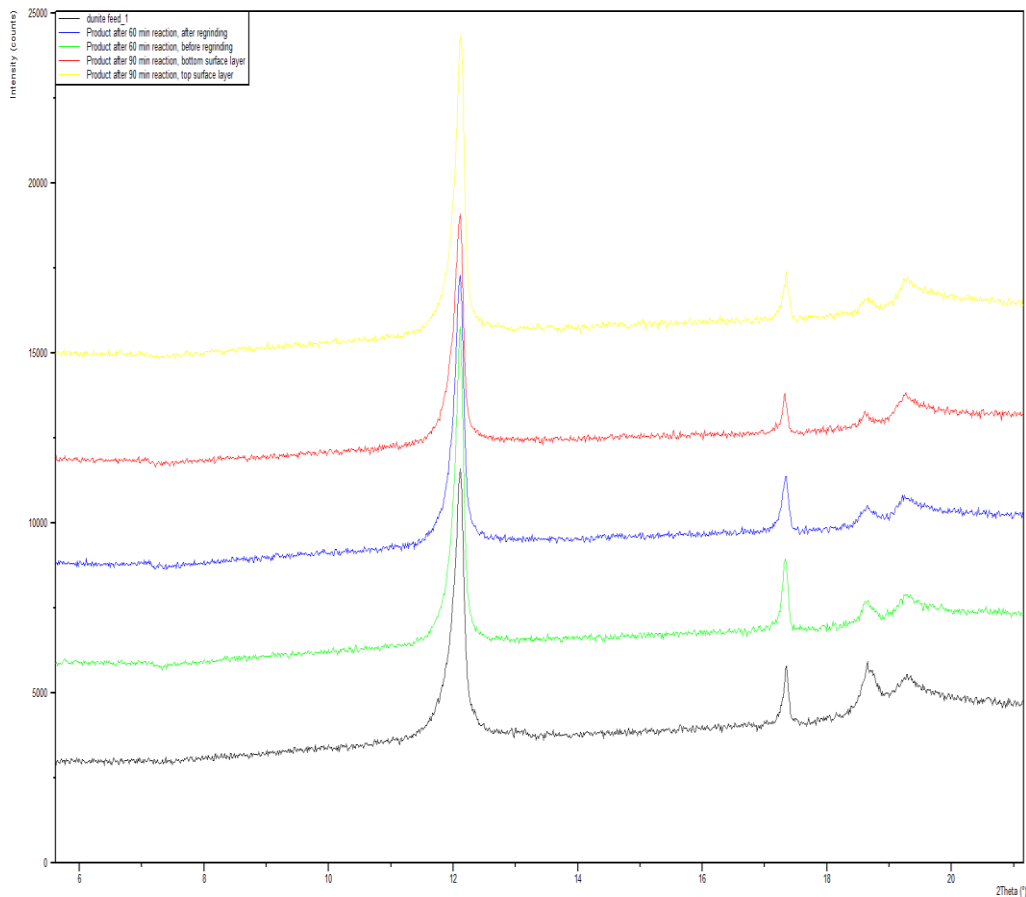
Fig. 9. Lizardite peak for all patterns (XRD)

4. CONCLUSION AND RECOMMENDATIONS

Increase in particle size is high in 60-90 min reaction and needles were observed after 90 min [1, 15], yield is low after first 60 min of reaction, hence olivine serpentinization may be occurring in the 60-90 minute reaction. It means lizardite seeding effect after regrinding. But why lizardite less at end of reaction, may be in second part of reaction, olivine is only serpentinizing to lizardite, not to magnesite. While grinding converted the lizardite to amorphous form or another form, hence it may started reaction or may be its amount is high and this reaction lizardite to magnesite has become more feasible. But yet its reactivity is less, so it reacted less, but still sufficient enough that its amount reduced from the amount present in the feed. Quantitative XRD or uniform grinded particles can tell the truth.

Nucleation and crystal growth seen on olivine surface after 1 h, fibres and needles start appearing on the olivine particles. Lizardite supersaturation level was achieved, may be nucleation started on olivine particles, which probably were broken to some extent by regrinding, but again major nucleation of serpentine on olivine surface. The morphology and sorting of the serpentine phases through the reaction cell suggest that crystallization of lizardite was controlled by heterogeneous nucleation on olivine under supersaturated conditions, and crystallization of chrysotile by nucleation on lizardite at higher levels of supersaturation [18], may be silica-rich layer they say is basically a lizardite formed from serpentinization of olivine, which when super-saturated cover the olivine surface and avoid its further reaction [1,9,12,13]. Hence, may be in next time, this lizardite is reacting instead of olivine. if lizardite is in a high quantity to become super-saturate quickly. After first hour of reaction, Lizardite settle on top and olivine settles on bottom, so may be separate lizardite from the top, after drying this slurry or without drying and heat activate only lizardite. No need to heat activate olivine, this

will save energy. Regrind olivine or both olivine and lizardite, mix them and again run the reaction.

One other important analysis is, may be magnesite is settling at the bottom, so doing seeding, increase magnesite cubes in size, now separate magnesite from bottom. This can save energy for regrinding, because we will not be regrinding the magnesite our product. May be use this magnesite, not 100% pure to seed next reaction. May be two reactor are running or two reactor can be used, the product from first is separated and then second reactor is running, with seeding. May be first reactor with seeding in batch mode, which is seeded by its own produced magnesite. Sell spare magnesite. Test these core concepts in pilot plant [10].

From particle size measurement, major increase in particle size because of this serpentinized lizardite formation was found. Further investigations by SEM and XRD were performed. Lizardite can be separated, needles were observed at the top and not at the bottom layer. May be we can do more research to separate lizardite (non-reactive) from olivine to made usage of dunite as an alternative feedstock. Similar happen in XRD, high peak intensity from top layer rather than bottom layer. Needles not observed after initial first hour reaction. More research required to figure out conditions under which this serpentinization can be avoided which seem to cause a major hinderance in utilization of worldwide dunite reserves (Chapter 8, silanol nests formation mechanism, research required [1]). Brucite was completely dissolved and converted to magnesite. It was not detected in XRD analysis of products and in TGA analysis no mass loss was determined.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Rashid MI. Mineral Carbonation of CO_2 using Alternative Feedstocks, The University of Newcastle, Australia; 2019.
2. Rashid MI, Benhelal E, Rafiq S. Reduction of Greenhouse Gas Emissions from Gas, Oil, and Coal Power Plants in Pakistan by Carbon Capture and Storage (CCS): A Review, Chemical Engineering & Technology. 2020;43(11):2140-2148.
3. Emad Benhelal JH. Guangyu Zhao, Muhammad Imran Rashid, Tim Oliver, Mark Rayson, Geoff Brent, Michael Stockenhuber, Eric Kennedy, Insights into chemical stability of Mg-silicates and silica in aqueous systems using 25Mg and 29Si solid-state MAS NMR spectroscopy: Applications for CO_2 capture and utilisation, Chemical Engineering Journal; 2020.
4. Farhang F, Oliver TK, Rayson M, Brent G, Stockenhuber M, Kennedy E. Experimental study on the precipitation of magnesite from thermally activated serpentine for CO_2 sequestration, Chemical Engineering Journa. 2016; 303(Supplement C):439-449.
5. Julcour C, Bourgeois F, Bonfils B, Benhamed I, Guyot F, Bodénan F, Petiot C, Gaucher É. Development of an attrition-leaching hybrid process for direct aqueous mineral carbonation, Chemical Engineering Journal. 2015;262:716-726.
6. Oliver TK, Farhang F, Hodgins TW, Rayson MS, Brent GF, Molloy TS, Stockenhuber M, Kennedy EM, CO_2 Capture Modeling Using Heat-Activated Serpentinite Slurries, Energy & Fuels. 2019;33(3):1753-1766.
7. Benhelal E, Oliver TK, Farhang F, Hook JM, Rayson MS, Brent GF, Stockenhuber M, Kennedy EM. Structure of Silica Polymers and Reaction Mechanism for Formation of Silica-Rich Precipitated Phases in Direct Aqueous Carbon Mineralization, Industrial & Engineering Chemistry Research. 2020;59(15):6828-6839.
8. Benhelal E, Rashid MI, Holt C, Rayson MS, Brent G, Hook JM, Stockenhuber M, Kennedy EM. The utilisation of feed and byproducts of mineral carbonation processes as pozzolanic cement replacements, Journal of Cleaner Production. 2018;186:499-513.
9. Rashid MI, Benhelal E, Farhang F, Oliver TK, Rayson MS, Brent GF, Stockenhuber M, Kennedy EM. Development of Concurrent grinding for application in aqueous mineral carbonation, Journal of Cleaner Production. 2019;212:151-161.
10. Benhelal E, Rashid MI, Rayson MS, Prigge JD, Molloy S, Brent GF, Cote A, Stockenhuber M, Kennedy EM. Study on mineral carbonation of heat activated

lizardite at pilot and laboratory scale, Journal of CO_2 Utilization. 2018;26:230-238.

11. Farhang F, Oliver TK. Rayson MS, Brent GF, Molloy TS, Stockenhuber M, Kennedy EM. Dissolution of heat activated serpentine for CO_2 sequestration: The effect of silica precipitation at different temperature and pH values, Journal of CO_2 Utilization. 2019;30:123-129.

12. Rashid MI, Benhelal E, Farhang F, Oliver TK, Stockenhuber M, Kennedy EM. Application of a concurrent grinding technique for two-stage aqueous mineral carbonation, Journal of CO_2 Utilization. 2020;42:101347.

13. Rashid MI, Benhelal E, Farhang F, Oliver TK, Stockenhuber M, Kennedy EM. Application of concurrent grinding in direct aqueous carbonation of magnesium silicates, Journal of CO_2 Utilization. 2021;48:101516.

14. Oliver TK, Dlugogorski BZ, Kennedy EM. Biologically enhanced degassing and precipitation of magnesium carbonates derived from bicarbonate solutions, Minerals Engineering. 2014; 61(0):113-120.

15. Rashid MI, Benhelal E, Farhang F, Oliver TK, Rayson MS, Brent GF, Stockenhuber M, Kennedy EM. ACEME: Direct Aqueous Mineral Carbonation of Dunite Rock, Environmental Progress & Sustainable Energy. 2019;38(3):e13075.

16. Rashid MIB, Farhang E, Stockenhuber F, Kennedy M, EM Magnesium Leachability of Mg-Silicate Peridotites: The Effect on Magnesite Yield of a Mineral Carbonation Process, Minerals. 2020;10:1091.

17. Swanson EJ, Fricker KJ, Sun M, Park AHA. Directed precipitation of hydrated and anhydrous magnesium carbonates for carbon storage, Physical Chemistry Chemical Physics. 2014;16(42):23440-23450.

18. Benhelal E, Rashid MI, Rayson MS, Brent GF, Oliver T, Stockenhuber M, Kennedy EM. Direct aqueous carbonation of heat activated serpentine: Discovery of undesirable side reactions reducing process efficiency, Applied Energy. 2019;242:1369-1382.