Study on hydro-alkali pre-treatment for red mud and the application of post-treated residue on construction materials

by

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OUTLINE

1. Overview of alumina industry in China
2. Phase transformation in hydro-alkali system
3. Introduction of three processes for treating RM
4. Utilization of post-treated RM for cement production
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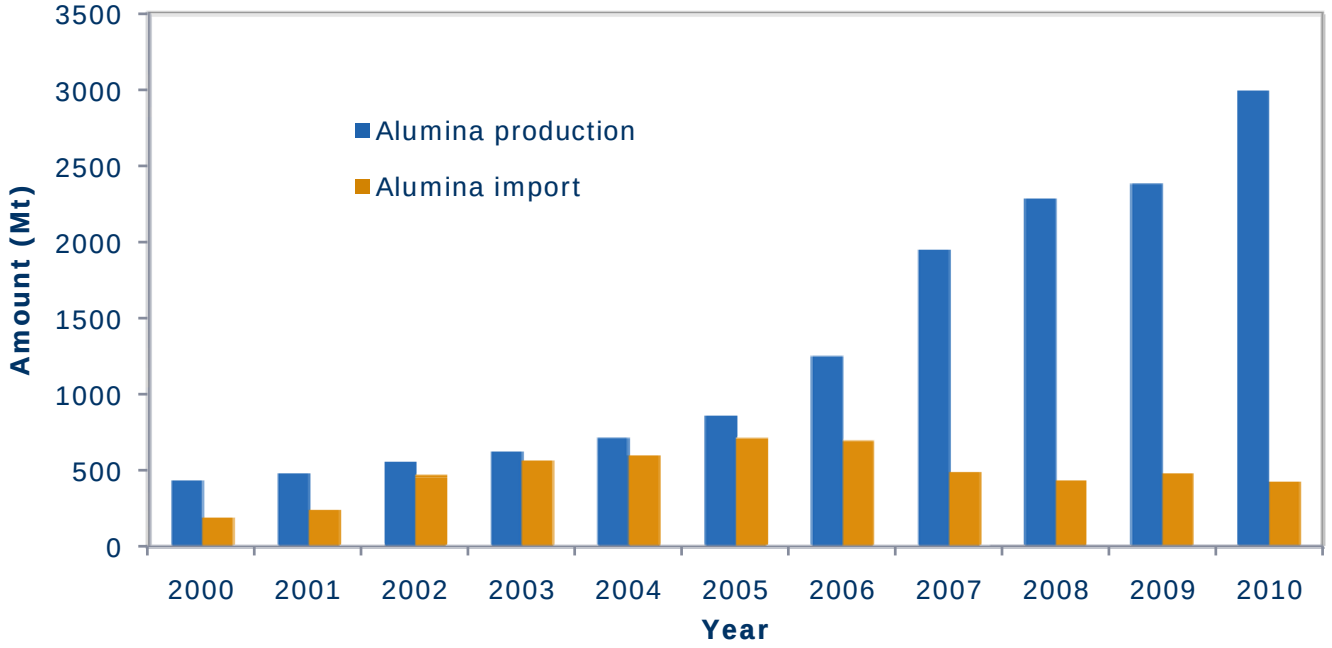
Overview of alumina industry in China

- Chinese alumina output had achieved **28.9 million** metric tonnes in 2010.

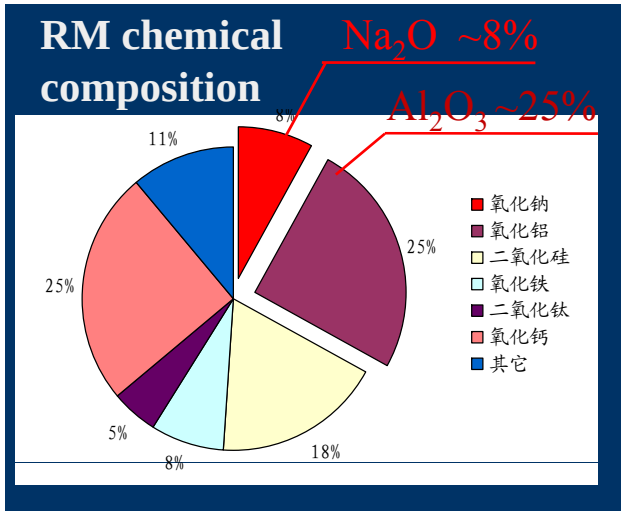


Overview of alumina industry in China

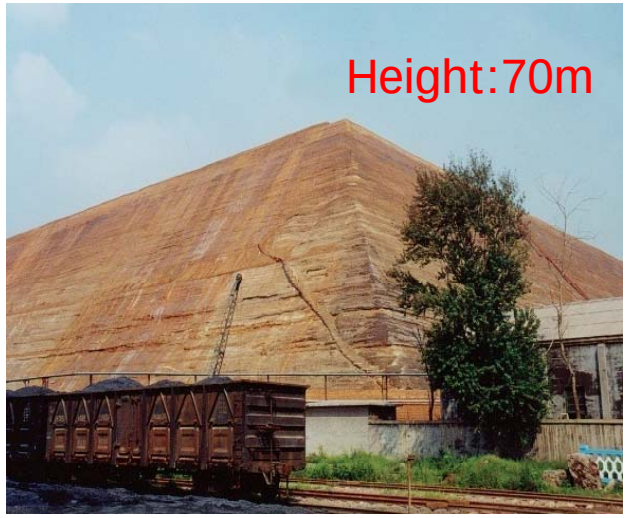
- **Bayer process** has been the major method in Chinese alumna production since 2005, and Sintering process is being eliminated step by step.

- It is estimated that Chinese alumina produced by imported gibbsite occupies about **1/3** of the total alumina output.

Overview of RM in China



- Output of RM reaches more than **30 million metric tonnes** every year, and the storage of RM **is ~250 million metric tonnes** in China.
- RM is difficult to utilize and has to be piled up



Red mud storage dam in China

Overview of RM in China

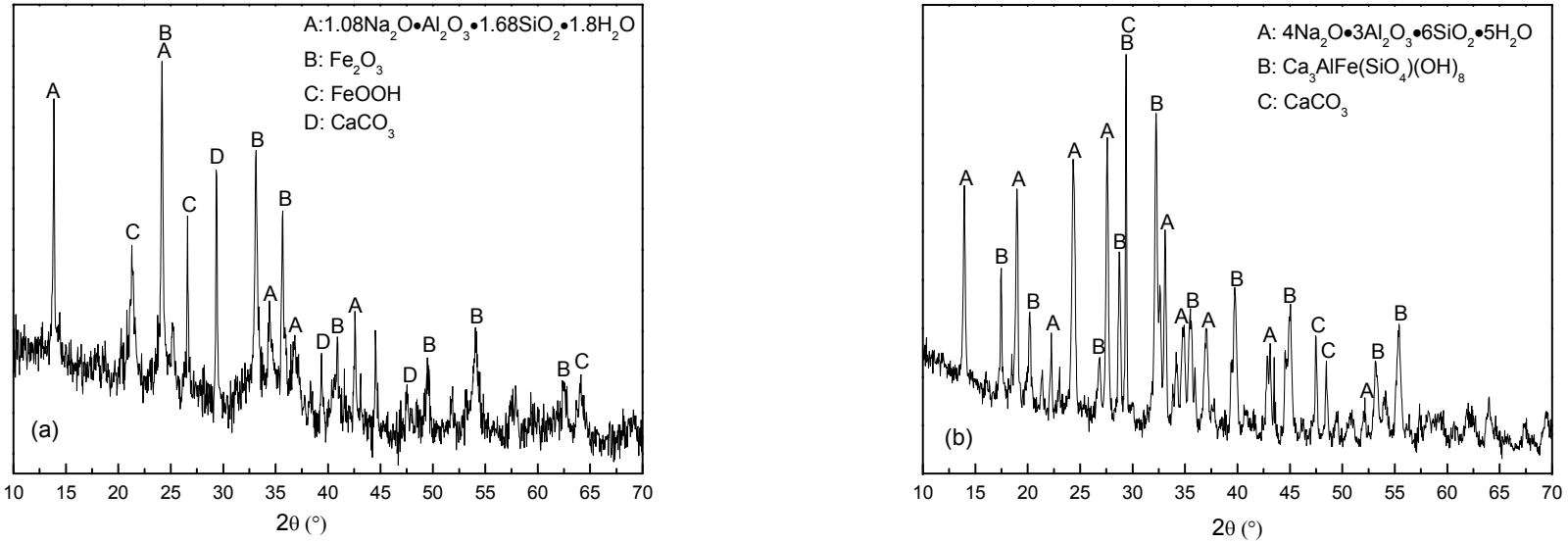
- **There are two distinctive RM existed in China generated from imported gibbsite and domestic dispore.**

Fe-lean generated from domsestic dispore, and Fe-rich RM from imported gibbsite

Overview of RM in China

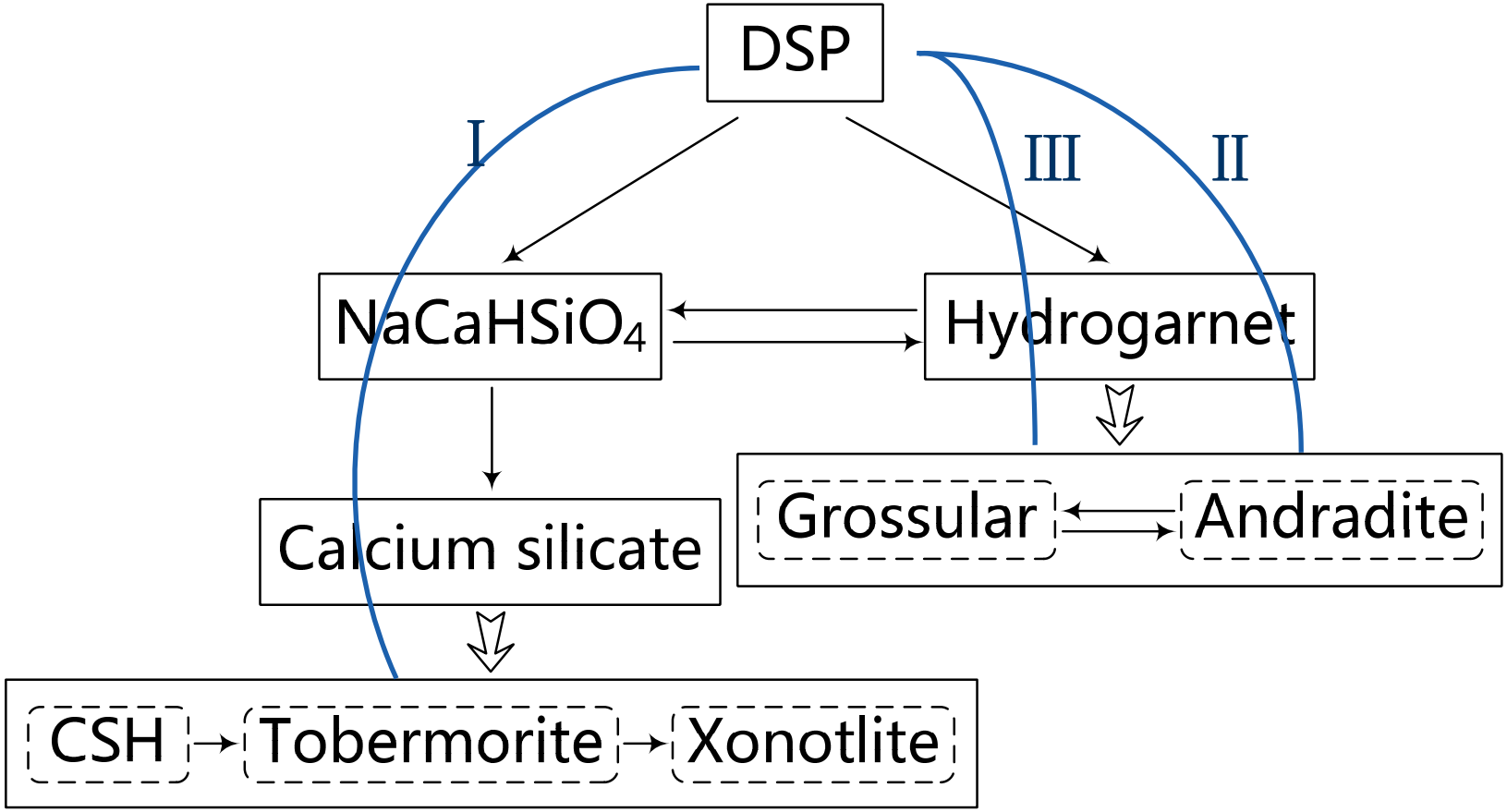
Table 1 Chemical compositions of RM tested(*wt%*)

	Na_2O	Al_2O_3	Fe_2O_3	SiO_2	CaO	TiO_2	A/S
Fe-rich RM	10.46	21.49	22.13	18.46	6.89	3.14	1.16
Fe-lean RM	8.22	23.80	6.46	18.97	18.00	5.16	1.25



XRD patterns of Fe-rich RM (a) and Fe-lean RM (b)

Phase transformation in hydro-alkali system



Phase transformation principle of RM in hydro-alkali system

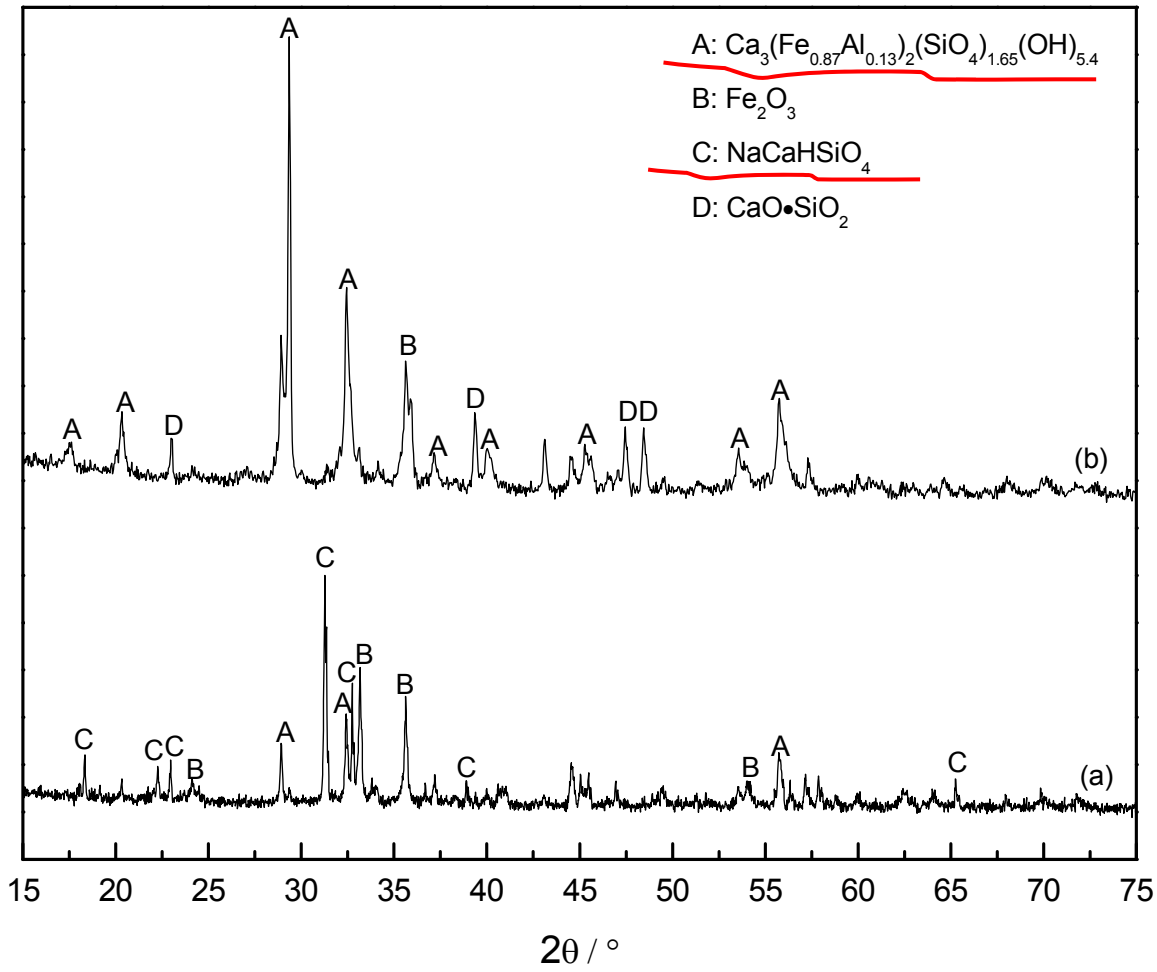
Introduction of three processes for treating RM

1、 **Mild hydro-chemical process**: DSP and/or Grossular → $NaCaHSiO_4$→Calcium silicate and/or hydrogarnet

Chemical compositions of post-treated residue of Fe-rich RM and Fe-lean RM by mild hydro-chemical process (*wt%*)

		Na_2O	Al_2O_3	Fe_2O_3	SiO_2	CaO	A/S
Fe-rich RM	de-alumina	10.42	4.77	23.07	14.42	20.53	**0.331**
	de-sodium	0.68	3.36	22.58	13.83	39.40	**0.326**
Fe-lean RM	de-alumina	11.51	6.30	7.95	21.86	22.48	**0.288**
	de-sodium	1.25	6.09	7.05	21.20	31.25	**0.274**

Introduction of three processes for treating RM



XRD patterns of post-treated residue of Fe-rich RM: (a) de-alumina residue, (b) de-sodium residue

Introduction of three processes for treating RM

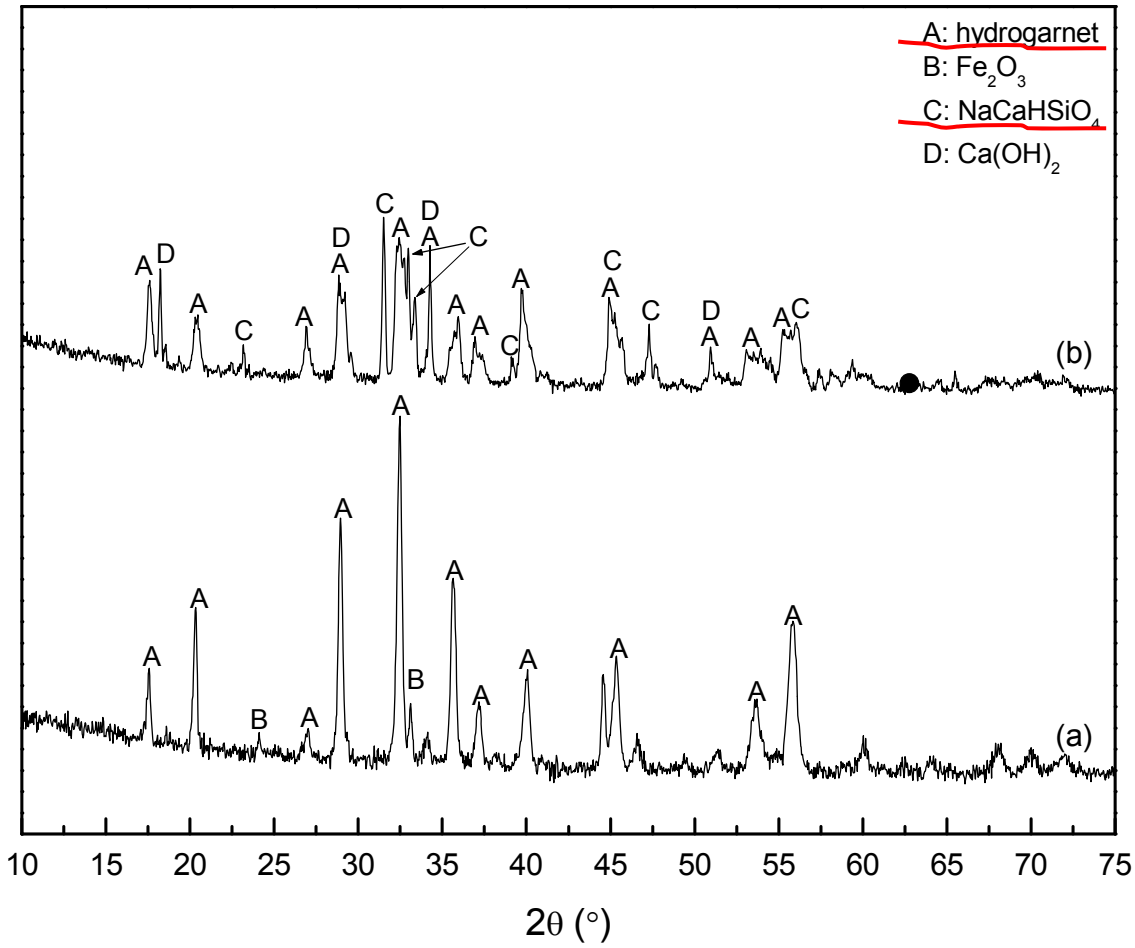
2、Hydrothermal process: DSP→ Andradite

- Treating raw RM

Chemical compositions of post-treated residue of Fe-rich and –lean RM by hydrothermal process (*wt%*)

	Na_2O	Al_2O_3	Fe_2O_3	SiO_2	CaO	TiO_2	A/S
Fe-rich RM	**0.44**	5.69	23.33	19.02	34.07	3.71	**0.288**
Fe-lean RM	3.30	12.49	5.21	15.11	35.54	3.92	**0.827**

Introduction of three processes for treating RM



XRD patterns of post-treated residue of Fe-rich RM (a) and Fe-lean RM (b) by hydrothermal process

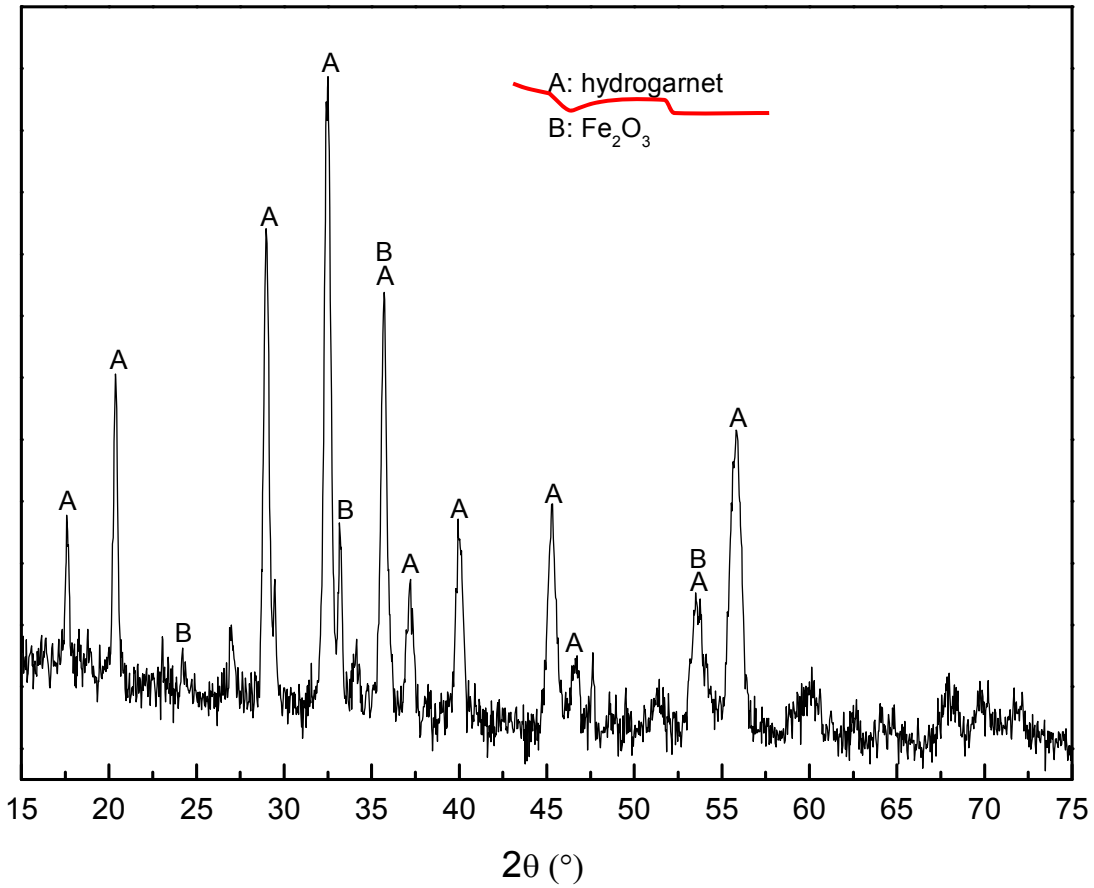
Introduction of three processes for treating RM

- Treating RM when adding enough reactive Fe

Chemical compositions of post-treated residue of Fe-lean RM after adding ferric hydroxide (*wt%*)

Na_2O	Al_2O_3	Fe_2O_3	SiO_2	CaO	TiO_2	A/S
1.25	5.94	21.24	13.09	31.60	4.58	0.454

Introduction of three processes for treating RM



XRD pattern of post-treated residue of Fe-enriched Fe-lean RM by hydrothermal process

Introduction of three processes for treating RM

3、Deeply de-sodium process

Chemical compositions of post-treated residue of Fe-rich and –lean RM by deeply de-sodium process (*wt%*)

	Na_2O	Al_2O_3	Fe_2O_3	SiO_2	CaO	TiO_2	A/S
Fe-rich RM	**0.23**	15.71	15.05	13.01	33.24	4.81	1.207
Fe-lean RM	**0.30**	18.35	4.78	13.51	37.60	4.93	1.358

Utilization of post-treated RM for cement production

● Raw materials

Chemical components of raw materials used in cement production (*wt%*)

	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2
limestone	42.05	2.79	0.75	0.49	51.19	1.82	0.20	0.04	0.15	0.05
shale	2.45	82.62	6.53	5.09	1.22	0.54	0.83	0.05	0.02	0.23
bauxite	6.96	54.12	29.13	4.98	1.08	0.31	1.47	0.33	0.02	1.49
Iron ore slag	2.99	49.33	3.07	36.85	4.25	2.41	0.18	0.07	0.04	0.14
1# RM	17.06	14.85	20.08	7.27	37.17	0.94	0.03	0.46	0.09	1.51
2# RM	18.04	16.87	7.19	10.46	42.55	1.56	0.00	0.95	0.10	2.36

1# RM: post-treated RM of Fe-lean RM by deeply de-sodium process,
2# RM: that by mild hydro-chemical process.

Utilization of post-treated RM for cement production

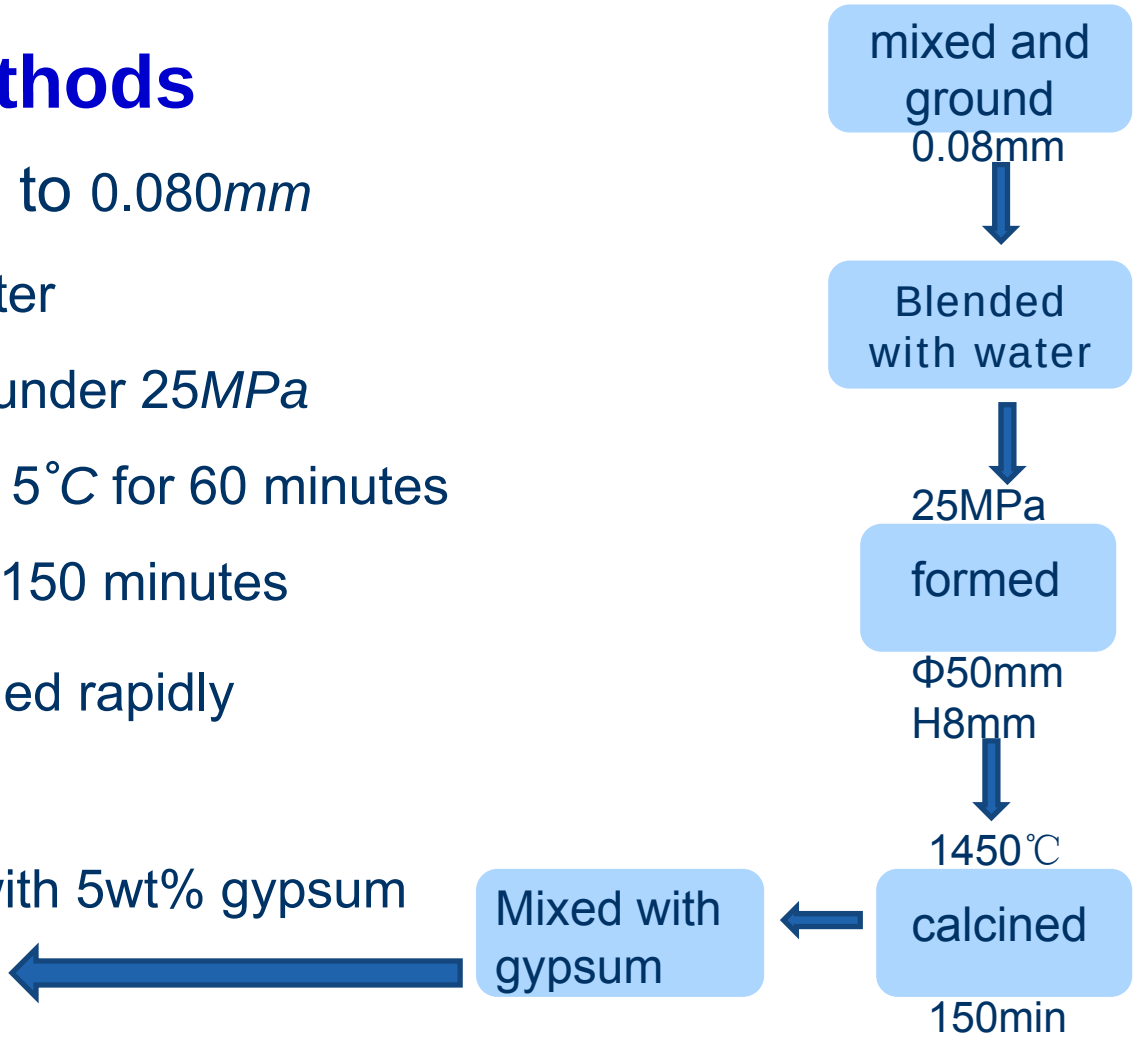
Ingredients of clinker raw meal and their rates

NO.	Ingredients of clinker raw meal, *wt%*						clinker rates		
	limestone	shale	bauxite	Iron ore slag	1# residue	2# residue	KH	SM	IM
1# clinker raw meal	75.67	12.16	0.00	1.68	**10.49**	0.00	0.89	2.47	1.48
2# clinker raw meal	72.12	9.11	5.43	0.00	0.00	**13.34**	0.87	2.39	1.48

Utilization of post-treated RM for cement production

•Preparation methods

- ground and seived to 0.080*mm*
- blended with 8*wt%* water
- formed in steel mould under 25*MPa*
- dried in oven at 105+/- 5˚*C* for 60 minutes
- calcined in 1450˚*C* for 150 minutes
- taken out and air-cooled rapidly
- Ground to clinker
- 95wt% clinker mixed with 5wt% gypsum
- the cement sample



Utilization of post-treated RM for cement production

- **Character determination**

f-CaO contents in clinkers prepared at different temperatures (*wt%*)

	1350˚C	1400˚C	1450˚C
1# cement clinker	7.77	3.99	1.74
2# cement clinker	3.30	1.35	0.45

Utilization of post-treated RM for cement production

cement samples (after flexural strength test)

NOTE: 1# and 2# was prepared by 1# and 2#clinkers, respectively

Utilization of post-treated RM for cement production

•Character determination

Physical properties of cement samples

	normal consistency (%)	Soundness	setting time (minutes)		flexural strength (MPa)		compressive strength (MPa)	
			initial	terminal	3 days	28 days	3 days	28 days
1# cement	23.69	qualified	110	225	4.5	8.7	21.6	53.2
2# cement	23.41	qualified	159	239	4.6	9.4	19.4	55

Utilization of post-treated RM for cement production

•Character determination

Specific radioactivity of cement samples and raw RM

	1# cement	2# cement	Requirements	Raw RM
internal exposure index (IRa)	**0.34**	**0.37**	1.0	1.9
external exposure index (Iy)	**0.55**	**0.78**	1.0	2.9

Conclusion

- Two distinct RM, i.e. Fe-rich and -lean RM exists abundantly in China which generated from imported gibbsite and domestic diaspore, respectively.

- The main phases in Fe-rich RM is DSP, while in Fe-lean RM are DSP and hydrogarnet (grossular).

Conclusion

•According to the principle, three pre-treat processes (mild hydro-chemical process, hydrothermal process and deeply de-sodium process) in hydro-alkali system were introduced for Fe-rich and -lean RM, respectively.

•The former two processes can recover sodium and alumina, while the last one can only recover sodium. All the three processes can reduce the sodium content to the level of about 1wt%. And A/S in the two former post-treated residues drops to below 0.5.

Conclusion

- Two kinds of post-treated residue of Fe-lean RM, dealt with mild hydro-chemical and deeply de-sodium processes respectively, were researched to produce cement.

- When post-treated residue accountes for above 10% of raw materials for producing cement clinker, the physical properties of both two kinds of cement produced by 95% such clinker and 5% gypsum meet the requirement of international cement 425 and match the criterion of radioactivity.

Thanks for your attention!

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