STUDY ON REMOVAL OF HIGH CONTENT OF SULFATE FROM BRINE WITH LIME PROCESS

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Abstract: In accordance with the phenomenon that extremely high content of SO_4^{2-} and Mg^{2+} in the brine of some mines afects salt quality, the authors make an experiment on the quaternary extraction brine in Dashanpu Mine.The brine is treated with relatively economical lime procee with certain effect achieved. Mg^{2+} and part of SO_4^{2-} can be removed simultaneously,however, SO_4^{2-} can not be removed thoroughly due to the restriction of solubility product of lime.In order to further remove content of SO_4^{2-},it needs to be combined with other treatment with a view to achieving ideal results with more economical treatment.

Key words: Lime process; brine treatment; sulfate radical

1 INTRODUCTION

In all parts of China, brine can be divided into type of mirabilite and type of plaster according to the major impurities in brine. The mirabilite type brine contains mainly Na_2SO_4 impurities and content of $CaSO_4$ is extremely low in the mirabilite type brine; the plaster type brine contains mainly $CaSO_4$ impurities. The quaternary extraction brine in Dashanpu Mine contains high $MgSO_4$, poor water quality, the content of SO_4^{2-} and Mg^{2+} is much higher than other similar brine. Because of high content of SO_4^{2-} and Mg^{2+} ,the consequences arising from a series of vicious, Such as: $MgSO_4$ and $MgCl_2$ enrich in the evaporator , so that the content of Cl^- in condensate is in a serious high, can not be effectively used; At the same time, because of two types of magnesium's enrichment, the production had to discharge mother liquor and cleaning equipment from time to time, which delays in production; It's difficult to deal with a large number of mother liquor,so it has to be back to the original wells to increase the content of magnesium in brine.Finnally, the quality of brine gets worse and causes a vicious cycle. if the mother liquor efflux,it will makes environmental pollution; more importantly, the impurities in finished products affected the quality of products seriously.

This shows that the content of SO_4^{2-} and Mg^{2+} in original brine is so high that it seriously affected the normal production. In order to avoid the adverse consequences of production, we deal with them from the source. The caustic soda and lime can be used treatment of Mg^{2+}; but the caustic soda can not remove the SO_4^{2-}, and the price is more expensive; if we use lime, due to slightly soluble calcium sulfate, it's feasible for removal of Mg^{2+} as well as removal of part of SO_4^{2-}. Comparison of two treatment methods, the author carried out using lime-site to remove high content SO_4^{2-} and Mg^{2+} in brine. The removal results of ions is discussed below, we are willing to discuss with colleagues to explore to find the most economical and reasonable method.

2 THE PRINCIPLE OF LIME PROCESS

2.1 Removal of Mg^{2+} with lime process

The principle of lime process to remove Mg^{2+} is that Mg^{2+} in brine react with OH^- in the lime to produce $Mg(OH)_2$ deposition, and the reaction equation is as follows:

$$Ca(OH)_2 + Mg^{2+} \rightarrow Mg(OH)_2\downarrow + Ca^{2+}$$

$$Ksp_{[Mg(OH)2]} = 1.8\times10^{-11}$$

Therefore, removal of magnesium are entirely feasible, it can be add in the form of milk of lime or lime powder.

2.2 Removal of $SO_4^{2-}$with lime process

Removal of SO_4^{2-} make use of Ca^{2+} in the lime and SO_4^{2-} in the brine to react to produce micro-insoluble $CaSO_4$ deposition. Because the solubility product of $Ca(OH)_2$ is not high, generated $CaSO_4$ is slightly soluble substances, both product solubility are in the same order of magnitude, with a very small difference, so Ca $(OH)_2$ and SO_4^{2-} reaction conducted in two steps: First, Ca $(OH)_2$ generate its own ionization Ca^{2+} and OH^-, free Ca^{2+} combined with SO_4^{2-} to generate $CaSO_4$, and the reaction equation is as follows:

$$Ca(OH)_2 \rightarrow Ca^{2+}+2OH^-$$

$$Ksp_{[Ca(OH)2]} = 5.5\times10^{-6}$$

$$Ca^{2+}+ SO_4^{2-} \rightarrow CaSO_4$$

$$Ksp_{[CaSO4]} = 9.1\times10^{-6}$$

From the above, we can see that it is limited by the lime own solubility product, removal of SO_4^{2-} is only partially removed with lime process, reaction should not continue after the reaction rate reaches a certain balance; and content of SO_4^{2-} in different get reaction rates in different .

3 THE EXPERIMENT FOR REMOVAL OF HIGH CONTENT OF SULFATE AND MAGNESIUM FROM BRINE WITH LIME PROCESS

3.1 Main composition of original brine

Tab. 1 Main composition of original brine

Name of material	Analyse item	Ca^{2+}	Mg^{2+}	SO_4^{2-}
Brine in Dashanpu Mine	content(g/L)	0.5	1.9	12.7
Mixed brine	content(g/L)	0.8	1.3	8.2

Annotate:The content of SO_4^{2-} and Mg^{2+} of quaternary extraction brine in Dashanpu Mine is high,we take it as raw material. The content of SO_4^{2-} and Mg^{2+} from Brine in Dashanpu Mine is higher than that of mixed brine.

We separately used milk of lime and lime powder to compare, the active ingredients are as follows:

Tab. 2 The active ingredients in milk of lime or lime powder

Name of material	lime powder	milk of lime
Content of CaO (%)	66	30

3.2 Experiment of adding lime according to different proportions

3.2.1 According to the theoretical value of 1:1, milk of lime is added in the raw brine, the result is as follows:

Annotate: One of the proportion of milk of lime is the ratio that theoretical value of content of Mg^{2+} will be reduced to lower than 0.5g / L and add milk of lime (or lime powder) actual amount, milk of lime (or lime powder) of components to CaO. The same below.

3.2.2 According to the theoretical value of 1:1 in the original brine add lime powder, the results are as follows:

Tab. 3 The major ion table before and after Milk of lime treatment

Type of brine		Dosing ratio	Ca^{2+} (g/L)	Mg^{2+} (g/L)	SO_4^{2-} (g/L)
Mixed brine	Before treatment	—	0.8	1.3	8.2
	After treatment	1: 1	2.0	0.4	7.5

Tab. 4 the major ion table before and after lime powder treatment

Type of brine		Dosing ratio	Ca^{2+} (g/L)	Mg^{2+} (g/L)	SO_4^{2-} (g/L)
Mixed brine	Before treatment	—	0.8	1.3	8.2
	After treatment	1：1	1.9	0.4	7.0

3.2.3 Excessive milk of lime is added to the original brine,the results are as follows:

Tab. 5 the major ion table before and after excessive milk of lime treatment

Type of brine		Dosing ratio	Ca^{2+} (g/L)	Mg^{2+} (g/L)	SO_4^{2-} (g/L)
Brine in Dashanpu Mine	Before treatment	—	0.5	1.9	12.3
	After treatment	excessive	1.7	0	7.6

From Tab. 5, add too much lime can removed Mg^{2+} in brine completely, but some of SO_4^{2-} content is only reduced from original 12.3g / L to 7.6g / L.

3.2.4 contrast Brine in Dashanpu Mine with mixed brine of the removal efficiency of $SO4^{2-}$

Tab. 6 comparison to ion removal efficiency

Type of brine	Type of lime	Dosing ratio	removal efficiency of Mg^{2+} (%)	removal efficiency of SO_4^{2-} (%)
Mixed brine	Lime powder	1：1	64.8	14.2
Mixed brine	Milk of lime	1：1	70.4	8.2
Brine in Dashanpu Mine	Milk of lime	excessive	100	38.2

From those Tab.s,we can see that according to the theoretical volume,add milk of lime to brine, removal rate of Mg^{2+} is good, but removal rate of SO_4^{2-} reached 14.2% only.
If added excessive milk of lime, removal rate of Mg^{2+} can reach 100%,but removal rate of SO_4^{2-} is only close to 40%. It seems that removal of SO_4^{2-} with lime process has a certain limit.

3.3 experiment in production site

To further verify the results, the authors did experiment in production siteaim at brine in Dashanpu Mine. The results are as follows: Test data showed that if add exessive limit, Mg^{2+} content in brine can be reduced to 0.5g/L, the removal rate is also as high as nearly 80%; but SO_4^{2-} removal rate is still only reached 33.3%, is close to the result of experiment in lab.

Tab. 7 The results of experiment in production site

Name of Samples	Mg^{2+} (g/L)	SO_4^{2-} (g/L)	removal efficiency of Mg^{2+} (%)	removal efficiency of SO_4^{2-} (%)
Brine from Dashanpu	1.9	12.3	—	—
Treatmented brine	0.4	8.2	79.4	33.3

3.4 Add calcium chloride experiment

The author did experiment once again that lime treatment remove SO_4^{2-} by brine in Dashanpu Mine, and then add different proportions of calcium chloride (No. 3 #, 4 #) in order to remove SO_4^{2-}, the results are as follows:

Tab. 8 Ions before and after lime and calcium chloride treatment

Number	Type of brine	Dosing ratio	Mg^{2+} (g/L)	SO_4^{2-} (g/L)
1#	Brine in Dashanpu Mine	—	1.9	12.3
2#	Brine afte lime treatment	excessive	0	7.9
3#	Brine afte calcium chloride treatment	1：1	0	2.5
4#	Brine afte calcium chloride treatment	A little excessive	0	2.0

From above we can see that when SO_4^{2-} content in brine is higher, it's more easy to remove SO_4^{2-} by adding calcium chloride.

4 DISCUSSED ABOUT BRINE TREATMENT STEP BY STEP

Because of brine in Dashanpu Mine with inferior quality and high content of SO_4^{2-}, it's impact a greater on the salt quality. To improve the salt quality,we should take effective and economic way to deal with brine .

Method 1: lime + barium chloride

As we all know,adding $BaCl_2$ can remove SO_4^{2-} in the brine completely, but the cost is too high. So it can be the first added lime to remove Mg2+ and SO_4^{2-} as much as possible, then continue to add $BaCl_2$ to reduced SO_4^{2-} to our requirement.

Method 2: lime + calcium chloride

This method is also taken step by step. First step, it can be added lime to remove Mg^{2+} and SO_4^{2-} as much as possible, and the second step, continue to add $BaCl_2$ to reduced SO_4^{2-} to our requirement. (It has been to verify as before 3.4).

Method 3: only add lime

This method only add lime to remove Mg^{2+} and SO_4^{2-} as much as possible, so the Glauber type brine is changed Mirabilite type brine.Brine evaporate until Na2SO4 of mother liquor to a certain extent concentration, we can deal with SO_4^{2-} in mother liquor.

By comparison with these methods, method 2 and method 3 one is obviously more economical than the method 1; but method 3 is also include the use of mother liquor. That which is the most economic way need to be further studied.

5 CONCLUSIONS AND RECOMMENDATIONS

To sum up, the use of lime can remove part of high content of SO_4^{2-} and Mg^{2+} in brine, the cost is lower when it achieve good results. However, it is limited by lime's own solubility product, SO_4^{2-} can only be removed to a certain extent.If we want to SO_4^{2-} is reduced to the requirements,we have to combine with other methods to deal with brine.

On the other hand, there will have much residue after the original brine is treated by lime, which is in the face of tremendous environmental pressures. If the residue can be separated and utilized well, it will be a good direction of development.In the future,we will further consider the separation and application of residue, in order to obtain a better response in the face of the growing economic and environmental pressures.

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