TECHNICAL DEVELOPMENT FOR PRODUCING K_2SO_4 BY COMPREHENSIVE UTILIZATION OF BRINE

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Abstract: This paper introduces the technical development of producing K_2SO_4 by comprehensive utilization of brine in the Potassium Sulfate Factory, Shandong Haihua Group Co. Ltd. Ten years efforts have improved the production process. The technical parameters in the factory are much better than the design targets. The factory is holding the market in severe competition conditions. Now the technology has successfully become a characteristic technology in producing K_2SO_4 by comprehensive utilization of brine in China.

Key words: Brine Potassium sulfate Comprehensive utilization

1. INTRODUCTION

The research for K_2SO_4 product began at 1980s. The consumption amount increased rapidly because of the excellent capability of K_2SO_4 and Chinese opening policy. A series of technologies for producing K_2SO_4 were developed. Only several processes such as Mannheim , comprehensive utilization of brine by hydrocyclone, Lop Nur comprehensive utilization of brine become the leading processes to produce K_2SO_4. This paper introduces the technical development of comprehensive utilization of brine by separating high temperature salt by hydrocyclone in Shandong Haihua Group Co. Ltd.

The production process of a factory which belongs to Haihua Group Co.Ltd was changed from producing KCl of 2500t./a to K_2SO_4 of 8000t./a by The Research Institute of Engineering Technology of CNPC who had developed the method of separation high temperature salt, cooperating with Shandong Haihua Group Co. Ltd in 1994. The design requirement of output and quality of the product was achieved at may 1994[1]. A new factory producing K_2SO_4 of 15000t/a was built in 1997 to replace the previous mentioned factory with further cooperation with above mentioned research institute. The output and quality of the new factory was achieved at 1998 by debugging production more than one year. At the same time, the consumption for raw materials and energy decrease greatly. The capability of producing K_2SO_4 in this way(The flow diagram of the process is shown in figure 1) is better than that produced by Mannheim method. This method does not have free acid .Its PH value in water is 7, containing Mg^{2+} of 0.4% (Mg^{2+} is a nutrition element for plant to synthesizing chlorophyll), which is more effective than the

Mannheim method. This process had acquired good economic and society benefit in last ten years.

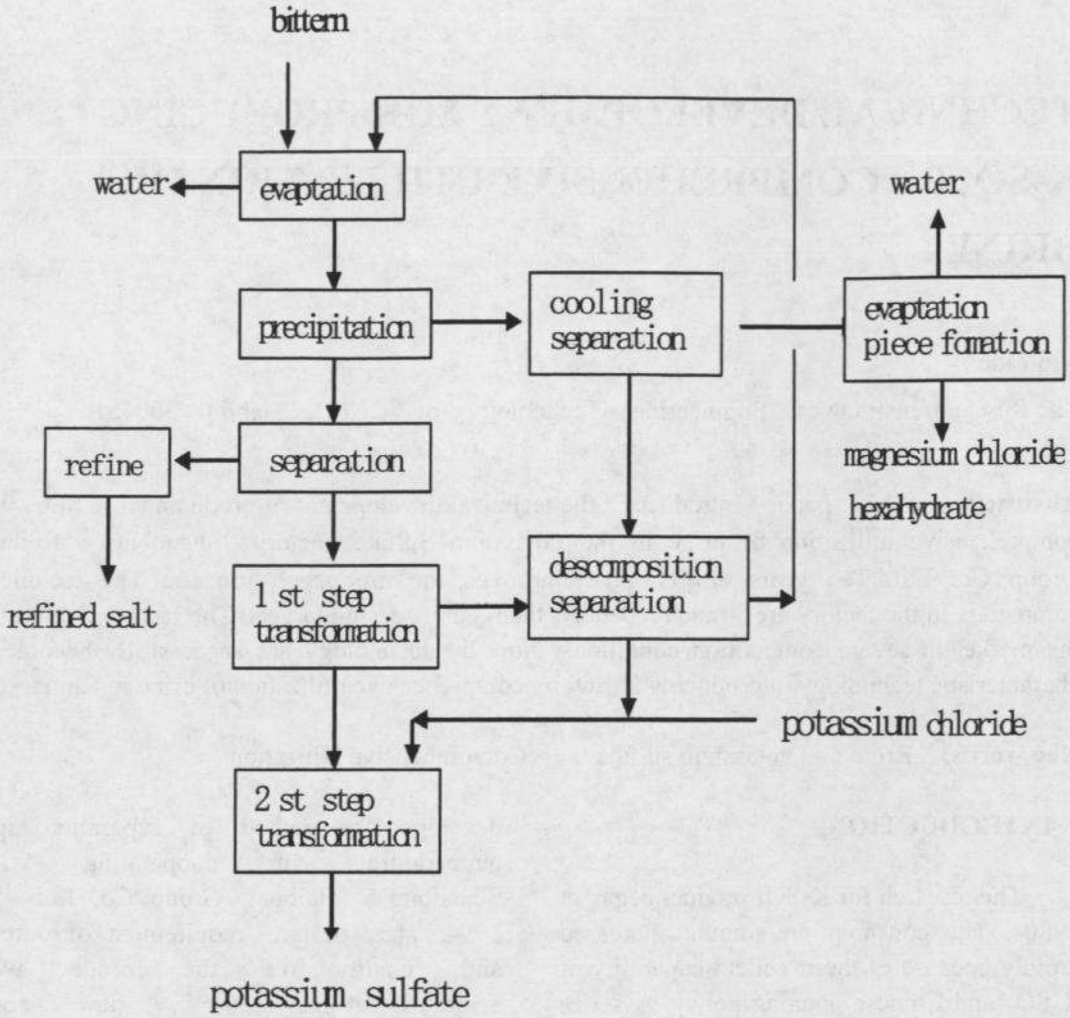

Figure 1. Flow diagram of process for producing K_2SO_4 by multi-purpose utilizing bitter brine

2.THE PRODUCTION OF THE NEW FACTORY IN LAST FIVE YEARS

(1) The output of potassium sulfate and by-product of industry-grade salt

The output for potassium sulfate and by-product of industry-grade salt in last five years is shown in table 1. The output for potassium sulfate in the successive five years exceeds 15000 t./a by 17%, 27%, 34%, 27%,42% respectively in 2002, 2003, 2004, 2005, 2006.

(2) Product quality

The product quality of potassium sulfate in last five years is referred in Table 2, and The product quality of by-product of industry-grade salt is referred in Table 3. It can be seen that the product quality of K_2SO_4

Table 1 The output of potassium sulfate and by-product of industry-grade salt

years	potassium sulfate (t)	by-product industry-grade salt (t)	production times (days)
2002	17560	17530	298
2003	19120	23100	313
2004	20110	25510	314
2005	19012	22079	276
2006	21253	23449	310

is better than Grade 1 of China standard on potassium sulfate for agriculture use, and the product quality of by-product of industry-grade salt is also better than Grade 2 of China standard for refined salt.

Table 2 The product quality of potassium sulfate in last five years

name of index	China standard on potassium sulfate for agriculture use (%)			examination result of really product (%)				
	excellent	Grade 1	Grade 2	2002	2003	2004	2005	2006
K_2O ≥	51.0	50.0	45.0	51.40	50.90	50.83	51.08	51.12
Cl- ≤	1.5	1.5	2.0	1.28	1.21	1.20	1.03	1.18
H_2O ≤	2.0	2.0	3.0	0.61	0.57	0.53	0.66	0.64

Table 3 The product quality of by-product industry-grade salt in lately five years

name of index	China standard for refined salt (%)			examination result of really product (%)				
	excellen	Grade 1	Grade 2	2002	2003	2004	2005	2006
NaCl ≥	99.10	98.50	97.50	97.43	97.55	98.41	98.22	98.10
H_2O ≤	0.30	0.50	0.81	0.55	0.46	0.48	0.45	0.46
Water insoluble ≤	0.05	0.10	0.20	--	--	0.08	0.07	0.09
Ca^{2+} +Mg^{2+} ≤	0.25	0.40	0.60	--	--	0.18	0.15	0.16
SO_4^{2-} ≤	0.30	0.50	0.90	--	--	0.42	0.36	0.40

(3) The consumption for main raw materials and energy

The consumptions for main raw materials and energy per ton of K_2SO_4 is referred in table 4(exclude the consumptions for producing bromine and $MgCl_2$•$6H_2O$). It can be seen that the consumption for brine is lower than design target in last five years, and the consumptions for steam and electric power are far lower than design target.

The consumption for KCl is higher than the design target because that concentration of brine is lower than 31 ºBe´, so the content of K^+ in brine is lower, In fact the rainfall were more in 2004 and 2006 in north of china .The quantity of brine which was used for production of K_2SO_4 increased constantly, which caused the shortage of raw brine. There is not enough time to solarize the raw brine. The content of KCl in brine is low. If convert the brine of 30 ºBe´ to 31 ºBe´, the energy

Table 4 The consumption for main raw materials and energy in lately five years (K_2SO_4/ton)

name of index	unit	2002	2003	2004	2005	2006	Design target
KCl (62% as K2O)	t	0.819	0.760	0.778	0.806	0.826	0.75
bittern	m3/°Be´	12.44/30.5	13.62/30.2	14.32/30	13.5/30.5	15.0/29.5	15.0/31
vapour	t	6.5	6.0	7.0	6.3	6.7	12.0
electric power	kW·h	230	197	187	182	181	300.0

Consumption of KCl, brine and vapour are shown in table 5, The consumption for KCl in table 5 is lower than design target of 0.75 ton. It will have the same result if we do in same way as for 2006.

(4) The output of by-product in the K_2SO_4 factory.

The by-product in K_2SO_4 factory are industry-grade salt and $MgCl_2$•6H2O. Its output per ton of K_2SO_4 in last five years is referred in table 6.

(5) The rates of recovery of various products(or molecule for NaCl)

We calculated the amount of input and output of K^+、Mg^{2+}、SO_4^{2-} and NaCl per ton of K_2SO_4 according to table 2、3、4、5 and the chemical composition in the table 7. Results of the rates of recovery of various products(or molecule for NaCl) are listed in the table 8.The rates of recovery of K^+、Mg^{2+}、$SO_4^{2-}$and NaCl have increased greatly in 2004 compare with that in 1994. Although the rates of recovery in 2004 still have gap with calculated value in theory, which are much higher compared with the traditional method of 60%～70%

Table 5 The consumption of K2SO4 factory in 2004 (conversing concentration of brine from 30 °Be´ to 31 °Be´)

name of index	KCl（62% as K2O）	brine	vapour
consumption	0.738t	12.26 m3（31 °Be´）	6.0t

Table 6 The output of by-product of industry-grade salt and $MgCl_2$•$6H_2O$ in last five years

Name for product	unit	2002	2003	2004	2005	2006
industry-grade salt	t	1.00	1.21	1.27	1.16	1.10
$MgCl_2$•$6H_2O$	t	3.64	4.24	4.46	4.16	4.45

Table 7 The chemical constitute of raw materials and products

Name form matter	ions (w.t.%)				compound (w.t.%)				
	K^+	Mg^{2+}	SO_4^{2-}	Cl^-	KCl	$MgCl_2$	NaCl	$MgSO_4$	K_2SO_4
bittern	0.65	4.30	4.78	15.15	1.23	12.11	9.14	5.99	0
potassium chloride	51.52	0.02	0.07	47.61	98.24	0	1.47	0.09	0
potassium sulfate	42.19	0.38	51.72	1.20	1.00	0.97	0	0.66	92.86
Magnesium chloride hexahydrate	0.06	12.08	1.09	35.44	0.12	46.24	1.57	1.36	0
industrygr ade salt	0.00	0.11	0.42	59.70	0	0	98.41	0.53	0

Table 8 The rates of recovery of K^+、Mg^{2+}、SO_4^{2-} and NaCl in 2004

Name form matter	unit	production results in practice		calculating value in theory
		2004	1994	
K^+	%	85.55	72.89	96.94
Mg^{2+}	%	87.45	77.00	97.44
SO_4^{2-}	%	75.49	54.21	86.59
NaCl	%	94.66	89.11	96.48

3. CONCLUSION

(1) The process for producing K_2SO_4 from brine developed by The Research Institute of Engineering Technology of CNPC has been successfully applied in Shandong Haihua Group Co. Ltd. The most important part of the process is separating high temperature salt by hydrocyclone. The output and quality of the new factory increases constantly and the consumption for the raw materials and energy decreases constantly, The process has become a method which can counterbalance with the Mannheim method.

(2)The quality of by-product of industry-grade salt has reached the standard of refined industry-grade salt by refining. Its value increases greatly. The competition ability of this process has enhanced

(3) This technology and another technology of separating high temperature salt by sedimentation centrifugal machine to produce MgSO4•6H_2O and industrial salt which was developed triumphantly by the author have realized the desire of comprehensive utilization of brine[2], which solved successfully the problems of running out of brine and had no polluting. High temperature salt changed from waste to usable goods, which had acquired good economic and society benefit.

(4) The consumption of energy for brine and KCl still have space to decrease by calculating the ions recovery rate of K_2SO_4 in 2004. The cost of K_2SO_4 will be reduced continuously by improve management, especially by reducing the times of washing to evaporator and reducing the loss of materiel when filtrating the high temperature salt slurry, which will further increase the economic benefit for the factory.

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