Ion Exchange Resins for Condensate Polishing in Air-cooled Ultra Super Critical Thermal Power Plants

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Abstract: Huadian Ningxia Lingwu Power Generation Co., Ltd. No.3 and No.4 Units (2×1,060MW) are the first 1,000MW class air-cooled ultra super critical power plants in the world. In air-cooled power plants, because the temperature of condensate is very high, mixed bed resin for condensate polishing (CP) requires high durability. For this requirement, high-crosslinked gel type cation exchange resin (CSK40) and porous type anion exchange resin (CPA12) were applied to CP in Huadian Ningxia Lingwu Power Generation Co., Ltd. No.3 and No.4 Units. The resins used in these power plants had still maintained high quality and performance after 3 years operation. Additionally, in the lab scale evaluation, CSK40 showed high oxidation resistant ability (durability), and CPA12 indicated superior PSS (Polystyrene sulfonate) adsorption capability which relates to the property of anti-organic-fouling. These results show the combination of CSK40 and CPA12 has high durability as mixed bed resins for CP. Therefore it is considered that this type of resin combination has high conformity to CP of air-cooled power plants in which the condensate temperature is very high and operating conditions are very sever for resins.

Key wards: air-cooled thermal power plant; condensate polishing; ion exchange resin; mixed bed; oxidation resistance

1. Introduction

In some areas of inland China, the water resource is insufficient. Air-cooled type coal-fired power plants with high water saving effect are suitable for such areas, and the introduction of air-cooled type plants is actually progressing. In air-cooled type power generation units, air is used as a coolant of condensers. Therefore air-cooled type units can save the consumption of water by about 70% as compared with water-cooled type units. However, in air-cooled type units, because the cooling effect of condensers is lower than that of water-cooled type, the temperature of condensate is relatively high and exceeds 60℃ in summer, and sometimes may reach about 80℃. [1.] Therefore, it can be said that conditions are very severe for ion exchange resins used in the condensate polishing (CP) system of air-cooled type power units.

In regards to the CP system of air-cooled type units, precoat filter of mixed powder resins have mainly been adopted to cope with such severe conditions in the past.[1.],[2.],[3.] With increases in the scale of power generation units, the required level of water quality will enhance and the importance of ion exchange resins for CP will also be higher and higher. Application of “precoat filter of powder resins + mixed bed” or “precoat filter of powder resins + cation bed + anion bed” as a CP system is recommended to the large-scale supercritical air-cooled power units.[3.]

Huadian Ningxia Lingwu Power Station No.3 and No.4 units (2×1,060MW) are the first 1,000MW class air-cooled ultra-supercritical power units in the world, which have “precoat filter of powder resins + mixed bed” as their CP system. With regard to mixed bed resins for CP of air-cooled power units, because the temperature of condensate is very high, good durability is required as well as high water-treatment ability. In these No.3 and No.4 units, high-crosslinked gel type cation exchange resin with good durability and porous type anion exchange resin, which has a property of anti-organic contamination (fouling), were applied and showed good quality and performance after 15, 25 and 34 months of operation.[4.],[5.],[6.] This report will introduce the time course of the quality and performance of these CP resins during 34 months of operation again and also present the consideration about their applicability to CP of air-cooled power units.

2. Operation situation of Linwu Power Station No.3 and No.4 units

The startup time of Linwu Power Station No.3 and No.4 units is in January and April of 2011, respectively. Concerning the CP system, there are four mixed bed vessels per one unit, and the two units share one set of resin regeneration equipment. The mixed bed of CP is basically operated as H-OH form. The temperature of condensate is: 55-60℃ in winter (from November to April), 65-75℃ in summer (from May to October).

3. Ion exchange resin to be applied

In air-cooled power units, since condensate temperature is very high and the operation condition of CP is severe to ion exchange resin, the combination of CSK40 and CPA12 was applied, which has good durability and high water-treatment ability. CSK40 is high-crosslinked (14%) gel type cation exchange resin with high oxidation-resistance and less leachables. CPA12 is porous type anion exchange resin with property of anti-organic contamination (fouling). This kind of resin combination has been applied in CP of PWR type nuclear power plants in Japan and high water quality has been achieved.

4. Resin samples for evaluation

The new resins and the resins taken from the plant were used as samples for evaluation. The sampling was carried out 4 times at the timing after 10, 15, 25 and 34 months of operation.

5. Evaluation items

The evaluation items are as follows:

- Ion exchange capacity
- Water content
- Particle size
- Uniformity coefficient
- Whole bead count
- Appearance
- Sphericity after osmotic-attrition (Mechanical strength)
- Eluting rate of PSS with high-M.W. (Cation resin)
  (PSS: polystyrene sulfonic acid)
- Oxidation elution test (Cation resin)
- Mass transfer coefficient (MTC)　(Anion resin)
- PSS adsorption capacity (Anion resin)

Eluting rate of PSS with high molecular weight (M.W.) (= PSS eluting rate) is an index for checking and comparing the degree of the oxidative degradation of cation resin, and its value increases with an increase in oxidation degree. The measurement method is as follows: put a certain amount of pre-treated cation resin into a certain amount of pure water, and incubate it at 80℃ with shaking for 20 hours. Then, measure the amount of PSS elution in the water phase by measuring absorbance (A225nm) and the ratio of high-M.W. PSS (M.W. $\geq$ 3,000) by gel permeation chromatography (GPC). Using these values, calculate the value of eluting rate of PSS with high-M.W. (mg/L-R・h).

Oxidation elution test is done to check the oxidation resistant ability (durability) of cation resins. Cation resins with high oxidation resistance show less leachables (= low △TOC) and low high-M.W. PSS ratio. The measurement method of oxidation eluting test is: put a certain amount of cation resin with iron-loaded (2g-Fe/L-R) into a certain amount of hydrogen peroxide solution, and incubate it at 40℃ with shaking for 24 hours (= oxidation treatment). Then, put the oxidized resin into a certain amount of pure water, and incubate it at 40℃ with shaking for 24 hours. After that, measure the TOC conc. and high-M.W. PSS ratio (M.W. ≥ 3,000, by GPC) in the water phase.

Mass transfer coefficient (MTC) and PSS adsorption capacity are the indexes for checking and compering the degree of surface contamination (organic fouling) of anion resin. PSS adsorption capacity can also show the anti-organic fouling property.

The measurement method of mass transfer coefficient is: put a certain amount of pre-treated anion resin into a column. Then, pass the raw water containing a certain conc. of Na_2SO_4 through resin layer at constant flow rate, and measure the conc. of SO_4^- in inlet and outlet water. After that, calculate the MTC value (m/s). MTC value becomes lower with surface contamination of anion resin becoming more severe. [7.]

PSS adsorption capacity was measured by dynamic adsorption method: put a certain amount of pre-treated anion resin into a column. Then, pass the raw water containing a certain conc. of PSS (e.g. M.W: 10,000) through resin layer at constant flow rate, and measure the conc. of PSS in outlet water. The total amount of PSS adsorption by resin at the timing when PSS conc. in outlet water reaches 50% of raw water's (at 50% leak) is defined as PSS adsorption capacity (mmol/L-R). The lower the PSS adsorption capacity value of used resin, the more severe the surface fouling. On the other hand, regarding new anion resin, high PSS adsorption capacity means high anti-organic fouling property.

6. Results and discussion

6.1 Change of quality and performance of cation resin CSK40

The analysis results of the cation resin samples (new resin and resin after 34 months operation) are shown in table 1. As for each analysis item, no significant change was seen after 34 months operation. Although ion exchange capacity decreased a little, the falling rate of ion exchange capacity after 34 months operation was only 3.4%. (fig.1)

Concerning the values of sphericity after osmotic-attrition (mechanical strength), there was no decrease after 34 months of operation — the mechanical strength was well maintained. (fig.2)

The value of PSS eluting rate gradually increased for an initial 15 months, but it decreased to very low level after 25 months of operation. (fig.3) We think the reason why the value of PSS eluting rate increased in the early period and then decreased, is that there was small amount of residual PSS in new resin particles and the residual

PSS was gradually eluted in early period, but the remaining PSS was almost completely released by the 15th month, then, the value of PSS eluting rate went down. Since the value was kept at a very low level after 34 months of operation, it is thought that the cation resin practically had not be oxidized, consequently, no deterioration of the quality and performance was not observed after 34 months operation.

From the above results, the cation exchange resin CSK40 maintained good quality and performance after about 3 years of operation in CP of air-cooled power units, therefore, results proved that CSK40 had high oxidation-resistant ability and good durability.

Table 1 Analysis results of quality and performance of cation resin CSK40 and anion resin CPA12 before and after use

Item	Unit	Cation Resin CSK40			Anion Resin CPA12		
		Spec	New Resin	34 Months	Spec	New Resin	34 Months
Ion Exchange Capacity	mmol/mL	⩾2.4	2.64	2.55	⩾1.2	1.33	1.16
Weakly Basic Capacity	mmol/mL	-	-	-	-	-	0.04
Water Content	%	29-39	34.6	33.9	45-55	51.9	52.6
Effective Size	mm	0.55-0.70	0.593	0.604	0.50-0.71	0.517	0.520
Uniformity Coefficient	-	⩽1.2	1.03	1.05	⩽1.4	1.30	1.31
Whole Bead count	%	⩾95	99	97	⩾95	99	98
Mechanical Strength	%	⩾90	99.56	98.92	⩾90	95.31	81.20
PSS eluting rate	mg/L-R/h	-	0.0012	0.0001	-	-	-
Mass Transfer Coefficent	×10^-5(m/s)	-	-	-	-	6.5	6.4
PSS Adsorption Capacity	mmol/L-R	-	-	-	-	0.16	0.18

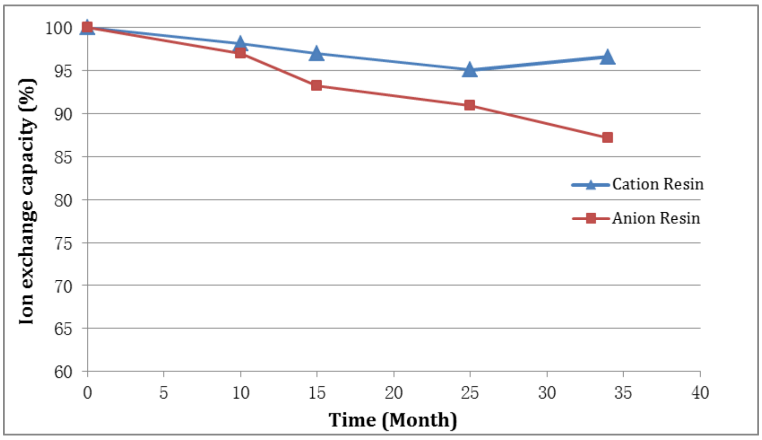

Fig. 1 Time course of ion exchange capacity of cation resin CSK40 and anion resin CPA12

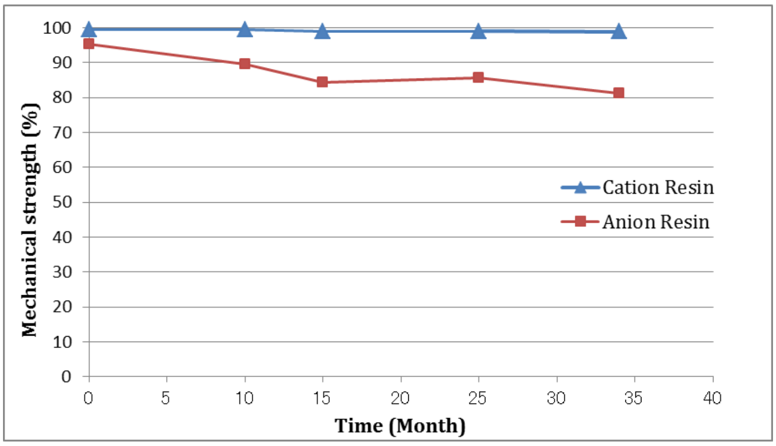

Fig.2 Time course of mechanical strength of cation resin CSK40 and anion resin CPA12

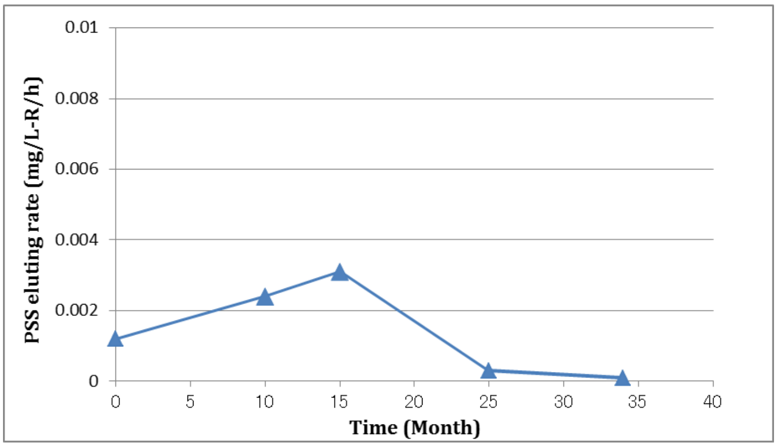

Fig.3 Time course of PSS eluting rate of cation resin CSK40

6.2 Change of quality and performance of anion resin CPA12

The analysis results of the anion resin samples (new resin and resin after 34 months operation) are shown in table 1. The gradual decline of ion exchange capacity was observed, and the falling rate after 34 months operation was 12.8%, as compared with new resin. (fig.1) It is thought that because condensate temperature of air-cooled power units is very high, the strongly basic anion exchange groups were decomposed by heating and turned into weakly basic anion exchange groups or completely lost their anion exchange capability.

The mechanical strength value slightly decreased in the early period of operation, but after that, it had been stably maintained around 80%. Moreover, regarding the resin strength, there was no practical problem after about 3 years of use. (fig.2)

The MTC value had been very stable and no big change was observed during 34 months operation. (fig.4) The PSS adsorption capacity value gradually decreased and reached about 44% of new resin's level after 15 months of operation. But after that, the value was stable for a certain period, and after 34 months of operation, it recovered to the same level as that of new resin (fig.4). It is thought that PSS adsorption capacity of anion resin gradually decreases during long time of use because of surface fouling by leachables eluted from cation resin. In this investigation, the decrease behavior of PSS adsorption capacity of anion resin (fig.4) accords with the increase behavior of PSS eluting rate of cation resin (fig.3). We think that, after that, the amount of PSS eluted from cation resin significantly decreased, as a result, PSS adsorption capacity recovered by repeated use and regeneration.

With regard to anion resin, since the heat-resistance of the strongly basic anion exchange group is low, in general, the reduction rate of anion exchange capacity relatively high. But the capacity of CPA12 still remained about 87%, even if it had been used under the high temperature condition of air-cooled power unit for about 3 years. Concerning the situation of organic fouling, although a certain reduction in PSS adsorption capacity was observed in the early period, MTC had been kept at high level all the time during operation. So it is considered no severe surface fouling had occurred during 34 months of operation.

On the whole, it can be said that anion resin CPA12 still maintained good quality and performance after about 3 years of use.

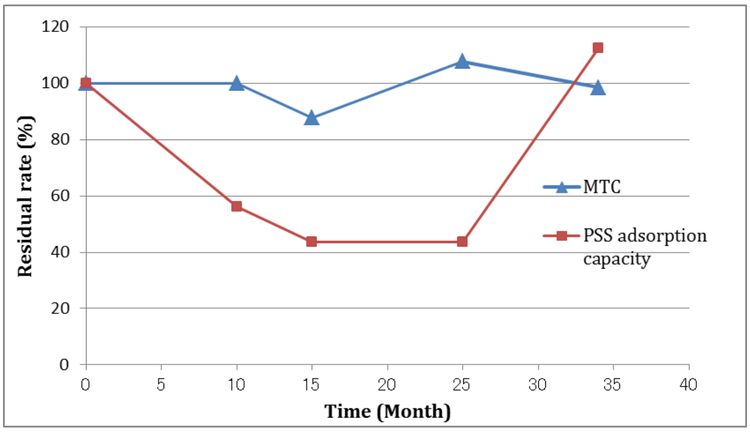

Fig.4 Surface contamination situation of anion resin CPA12 during 34 months operation. (Time course of MTC and PSS adsorption capacity.)

6.3 Observation of appearance

The appearance pictures of cation and anion resins before use and after 34 months use are shown in Fig.5. Both resins maintained good appearance after 34 months of use, and a noticeable deterioration in appearance such as cracks or breaking of resin particles was not observed.

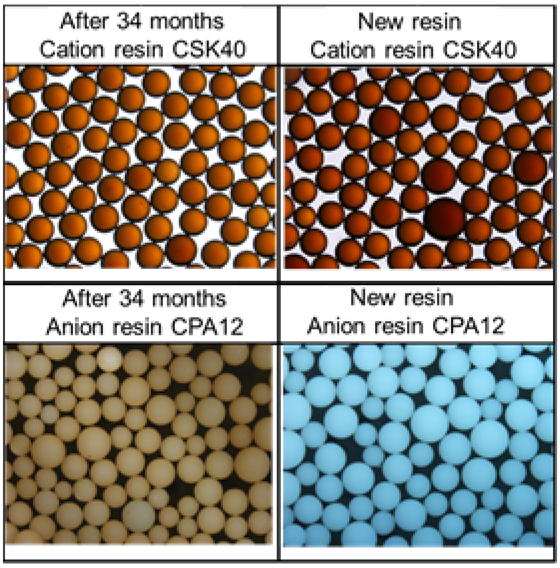

Fig.5 Appearance of cation and anion resins before use and after 34 months use

6.4 Quality of CP outlet water

The quality of CP outlet water of both No.3 and No.4 units had met water quality control standard (table 2) during 34 months operation, and there had been no problem about demineralization performance of CP.

Table 2 Quality standard of CP outlet water (DL/T912-2005 Quality criterion of water and steam for supercritical pressure units in fossil-fired power plant)

	Cation Conductivity (25℃) (μS/cm)		Silica (μg/L)	Fe (μg/L)	Cu (μg/L)	Na (μg/L)	Cl^- (μg/L)
	AVT	OT					
Standard	<0.15	<0.12	⩽10	⩽5	⩽2	⩽3	⩽3
Desired	<0.10	<0.10	⩽5	⩽3	⩽1	⩽1	⩽1

6.5 Lab evaluation of oxidation resistant ability (durability) of cation resin CSK40 and PSS adsorption capacity (anti-organic fouling property) of anion resin CPA12

The oxidation elution test was conducted using new sample of CSK40 (gel type, 14% cross-linkage) and other gel type resin samples (cross-linkage degree: 8%, 10%, 16%) at the lab in order to verify the superiority of oxidation resistant ability (durability) of CSK40. The result is shown in Fig.6. The △TOC value and high-M.W. PSS ratio of

CSK40 after oxidation treatment was controlled at very low level. It means CSK40 has high oxidation resistant ability (durability).

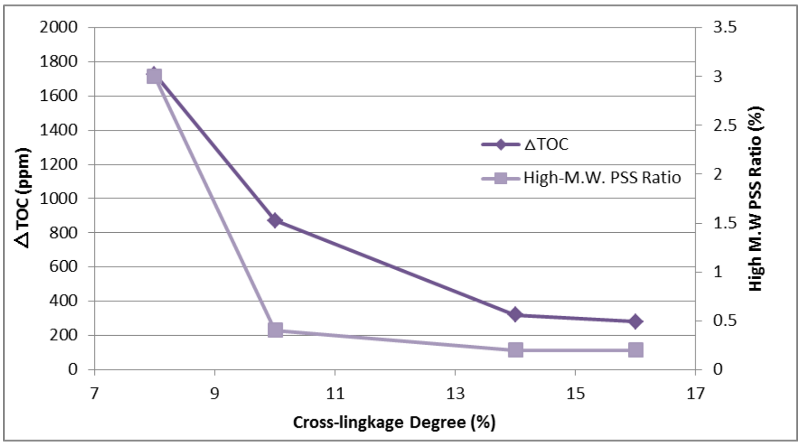

Fig.6 Oxidation resistant ability of cation resin CSK40 with 14% cross-linkage (Cross-linkage degree vs. leachables after oxidation treatment)

Regarding the anti-organic fouling property of anion resin CPA12 (porous type, meddle cross-linkage), its PSS adsorption capacity value was compared with the values of gel type anion resin (middle cross-linkage) and highly porous type anion resin (high cross-linkage). The result is shown in Fig.7. Porous type anion resin CPA12 showed much higher PSS adsorption capacity than gel type and highly porous type anion resins. Therefore, it is proved that CPA12 has superior anti-organic fouling property.

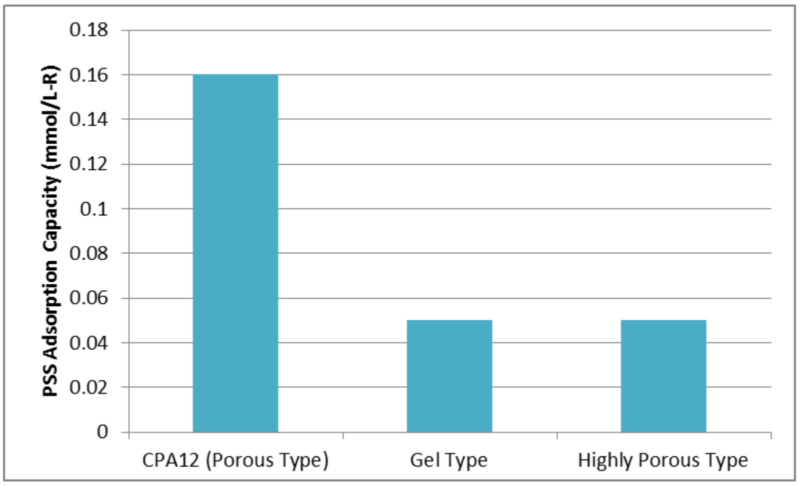

Fig.7 comparison of PSS adsorption capacity among CPA12 (porous type), gel type and highly porous type anion resins

7. Conclusion

In Huadian Ningxia Lingwu Power Station No.3 and No.4 units (2×1,060MW, air-cooled type), high-crosslinked gel type cation exchange resin CSK40 and porous type anion exchange resin CPA12 were applied for their CP systems. Resin samples were taken out after 10, 15, 25 and 34 months of operation, and the analysis of each sample was carried out. And lab evaluation was also conducted with new resins in order to verify the superiority of CSK40 in oxidation resistant ability (durability) and CPA12 in anti-organic fouling property.

Cation resin maintained good quality and performance after 34 months of operation, and the decreasing rate of ion exchange capacity after 34 months operation was 3.4%

Regarding anion resin, the ion exchange capacity decreased 12.8% after 34 months of operation. Although PSS adsorption capacity decreased in the early period, it recovered to the original level in the latter period, and a decrease of MTC values was not observed all the time during 34 months operation. Therefore it is considered that the surface contamination (organic fouling) did not occur during 34 months of operation. Since the porous type anion resin has a property of anti-organic fouling, and cation resin used together has high oxidation resistant ability and less leachables, the quality and performance of anion resin had not been affected by organic fouling even after 34 months of operation.

From the consideration about resin analysis results and CP outlet water quality, the resins applied in CP of No.3 and No.4 units still maintained good quality and performance after 34 months of operation.

The results of lab evaluation also show that cation resin CSK40 has high oxidation resistant ability (durability), and anion resin CPA12 has superior PSS adsorption capacity (anti-organic fouling property).

As a result of analysis of used resins taken from the actual air-cooled power plant and lab evaluation of new resins, it is considered that combination of high cross-linked gel type cation resin CSK40 and porous type anion resin CPA12 has high durability as mixed bed resins, and also has a high conformity to CP of air-cooled power plants in which the condensate temperature is very high and operating conditions are very sever for resins.

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