



# Operating Steam Generator Blowdown Demineralizers in the Amine Form

This Technical Paper discusses factors that impact operating efficiency of a SGBD demineralizer when ETA and MPA amines are present in the system.

Prepared by Terrence Heller of Ecolab Corporation for the 2013 EPRI condensate polishing workshop in Seattle, Washington.

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# Abstract

A steam generator blowdown (SGBD) demineralizer removes unwanted ions such as sodium ( $\text{Na}^+$ ) and corrosion products for the steam generator. This minimizes both potential corrosive activities in the system and deposits on heat transfer surfaces while allowing purified water to be reused. During purification the SGBD demineralizer resin also loads with useful amines that protect the condensate system. Operating the ion exchange bed in an amine form not only reduces loss of this amine chemistry but also removes sodium and ensures pure water is returned to the steam generator. Operating in the amine form reduces costly waste and saves time at the site. This report discusses factors that impact operating efficiency of a SGBD demineralizer when ETA and MPA amines are present in the system.

## Introduction

Pressurized water reactor SGBD systems are designed to purify water from all steam generators within a unit and return blowdown to a hot well or where condensate and make-up are collected. This combined feedwater is then returned back to the steam generator (SG).

Blowdown demineralizers remove corrosion products and low-level impurities that support corrosion. These impurities include sodium ( $\text{Na}^+$ ), chloride ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) from sources such as makeup water, resins and treatment chemicals. Conditioning chemistries such as Morpholine, 3-methoxypropylamine (MPA), Dimethyl amine (DMA) and monoethanolamine (ETA) help minimize corrosion and reduce iron transport from the turbine and condensate system. These amines, along with ammonia—the degradation product from hydrazine—contribute to cation loading and compete with sodium for cation resin exchange sites. Hydrazine, an oxygen scavenger, will also contribute Hydrazinium to cation loading, which can impact equilibrium leakage when first fed to the system. Best practice is to bypass demineralizers prior to initial feed of hydrazine and resume demineralizer operation when hydrazine concentration stabilizes.

The Electric Power Research Institute's (EPRI) guideline for steam generator sodium is 5.0 ppb; the Institute of Nuclear Power Operations (INPO) has established a rating system, the Chemistry Effectiveness Index (CEI), where plants are given favorable performance ratings when sodium is maintained below 0.8 ppb. An action level of 0.5 ppb is now strongly held by the industry. This factor drives SGBD and condensate polishing operations.

SGBD demineralizer designs vary. Deep beds consist of one to three vessels with flexibility of operating in parallel, series or separately. Practices include operating only one polisher vessel with one in standby, or a lead lag configuration. Single bed operations may be regenerated.

Non-regenerable systems generally have two vessels online in series with strong acid cation (SAC) resin in the lead vessel(s) and mixed bed resins (MB) in the second or lag vessel. Vessel size and service flow also varies, resulting in a range of service time. Non-regenerable systems generally operate a lead cation in H<sup>+</sup> form until it reaches an amine break. At this point some operations will replace this lead bed. When replacing resin at the amine break, the lead cation bed will last 1–2 weeks. The second vessel loaded with layered or mixed bed resin will operate longer, possibly up to 12 months. When only a single vessel is in service, the practice is to layer cation and anion in the vessel or use a mixed bed. The beds are cation rich in both situations, with 2 or 4 to 1 equivalence of cation to anion.

An important factor affecting life of SGBD resin is in-leakage from either makeup water system, condensers or from primary to secondary leaks. Condenser leaks are addressed by deep bed condensate polisher, if available. If in-leaking is present, a SGBD demineralizer must be operate in H-OH form and primarily in 2:1 or 1:1 chemical equivalence to optimize bed life. With a primary to secondary leak, the resin will be handled as radwaste. If in-leakage is not present, it is possible to modify the SGBD demineralizer to operate in an amine form, which will significantly extend resin life and reduce amine feed.

## Discussion

Operating in amine form is less common due to concern of elevating Na<sup>+</sup> in the SG. A few U.S. plants operate the SAC and/or MB in the amine form and replace resin at a Na<sup>+</sup> break. If beds start in the H<sup>+</sup> form, the lead bed will pass amine in approximately two weeks, then continue in service 60 to 90 days to a Na<sup>+</sup> break. The mixed bed passes amine in another 10 days, then operates for another 30 to near 60 days to the Na<sup>+</sup> break. When passing the amine break, effluent Na<sup>+</sup> may increase slightly to approach 0.2 ppb (based on plant conditions) and then drop back to a steady state until reaching a Na<sup>+</sup> break, which is generally 0.4 ppb. European plants operate SGBD demineralizers up to 18 months. However, in Europe it is common to run Na<sup>+</sup> level in the SG up to 2 ppb.

Operating resin supplied in the amine form will eliminate the amine break as well as the sodium excursion at the amine break. The beds will operate to an equivalent throughput as H<sup>+</sup> form resin when operated to the Na<sup>+</sup> break. Service time for blowdown demineralizers operated to the Na<sup>+</sup> break will be dependent on service flow, volume and configuration of resin, sodium endpoint chosen, amine chemistry and ammonia levels in the SG.

When operating in amine form, all exhausted resin in the blowdown vessel must be completely removed before loading new resin. Old resin may contribute impurities (e.g., Na<sup>+</sup> and Cl<sup>-</sup>), especially when passing the amine break. Also, when systems operate at elevated pH (e.g., 10) leakage of Na<sup>+</sup> and Cl<sup>-</sup> will be greater than plants operating at lower pH (e.g., 9). Low level Cl<sup>-</sup> release in a few cases may not be a problem as NH<sub>4</sub>Cl is sometimes added to control caustic in crevices. Finally, older cation resin may also release sulfate.

SGBD demineralizer systems have effectively used Strong Acid Cation (SAC) gel resins with 8–10% crosslinking mixed with non-porous Strongly Basic Anions (SBA) gel resin. However, the current trend is to use gel SAC resins with higher capacity and higher crosslinking. Anion capacity is not a limiting factor unless a leak occurs. Total anion capacity in clean systems generally can be reduced and offset with SAC to extend the mixed bed life. Increased cross-linking of the gel SAC resin allows for increased operating capacity. More importantly, this increases SAC resin selectivity for Na<sup>+</sup> resulting in lower leakage. Increasing cation capacity increases selectivity for Na<sup>+</sup> over amines (e.g., MPA and ETA to a lesser degree) while selectivity for Na<sup>+</sup> over ammonia drops slightly. Na<sup>+</sup> selectivity increases as amines concentration on the resin increases, but as ammonia on the resin increases, Na<sup>+</sup> leakage increases and cation operating life decreases. Studies by EDF in France found Na<sup>+</sup> loading was only 0.2 – 0.8% of SAC capacity when the steam generator reached the allowed level of 2.0ppb Na<sup>+</sup>.

Gel SAC resins are known for higher volumetric capacity (i.e., capacity calculated based on the wet volume of resin) and generally are lower in cost than macroporous resins. Gel resins have a uniform matrix as well as uniformity of functional groups throughout the bead. Therefore, as SAC cross-linking increases capacity increases and bead surface area to total capacity decreases.

Macroporous SAC resins are high in cross linking and have a much greater surface area to capacity ratio. High capacity macroporous SAC resins offer a unique balance considering the competition for functional sites and limited Na<sup>+</sup> loading that occurs. One study<sup>7</sup>, supported greater operating capacity for the macroporous cations resin over high capacity gel resins. European plants (e.g., EDF units) have preferred this macroporous resin over gel type.

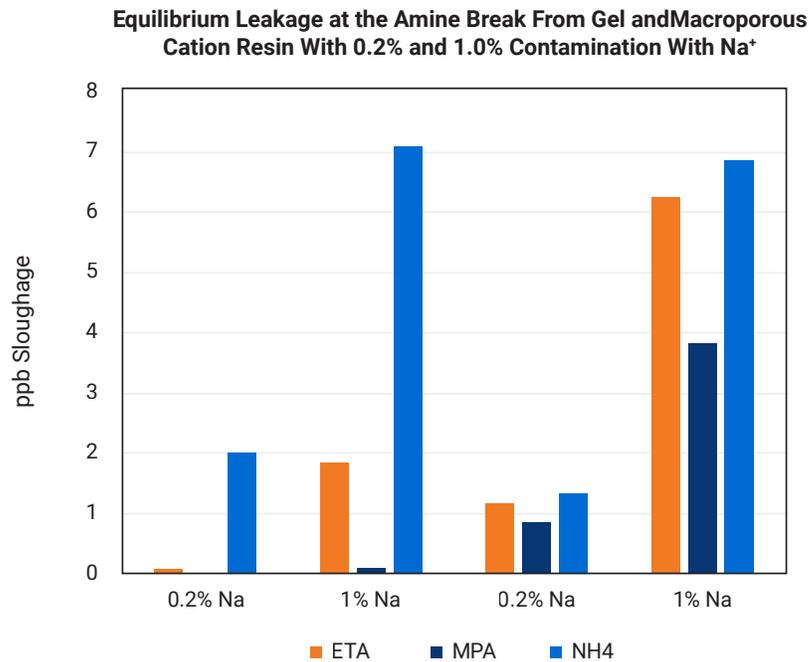
During the service cycle resin leakage (ions leaving the resin bed) is driven by physical and chemical forces both inside and outside of the resin bead. These forces will impact the resin ability to hold ions and remove ions from the influent water. Those impurities passing an ion exchange bed are impacted by two types of leakage, equilibrium and kinetic. Equilibrium leakage occurs when ions that are on the resin migrates off when subjected to an environmental change. This equilibrium leakage is represented by a Na<sup>+</sup> excursion when operating a cation resin past the amine break. Kinetic leakage is represented by a small percentage of ions passing through the exchange bed that are not picked up by the resin. Kinetic leakage will likely be a negligible driver determining resin service life in the steam generator blowdown demineralizer.

Equilibrium leakage will likely be the greater driver determining resin service life. When new (or regenerated) resin is installed and operated past the amine break there is a level of Na<sup>+</sup> that leaves the resin as equilibrium leakage. Selectivity of the resin (ability to hold Na<sup>+</sup> over amine) will impact the level of leakage at the amine break. Residual Na<sup>+</sup> ions are pushed through the bed ahead of the advancing amine front resulting in a peaking of Na<sup>+</sup> as the front reaches the exit of the bed. Lower Na<sup>+</sup> on the virgin resin will therefore result in a shorter duration and lower level of Na<sup>+</sup> excursion.

The actual concentration of  $\text{Na}^+$  exiting the resin bed will depend on a number of factors including the amount of  $\text{Na}^+$  remaining on the resin as supplied by the manufacturer (or after regeneration), the amine chemistry used in the system, and type of resin used ( Figure 1 ). The  $\text{Na}^+$  leakage in the presence of ammonia is slightly greater from the macroporous SAC verses the gel. This is observed for both the 0.2% and 1% levels of  $\text{Na}^+$  cross contamination on the resin. On the other hand,  $\text{Na}^+$  leakage in the presence of MPA and ETA is significantly lower for the macroporous verses the gel.  $\text{Na}^+$  leakage from the macroporous SAC in the presence of ETA was approximately 35% of that for the gel SAC; for MPA it was just 5%.

**FIGURE 1**

**Equilibrium Leakage at the Amine Break From Gel and Macroporous Cation Resin With 0.2% and 1.0% Contamination With  $\text{Na}^+$**

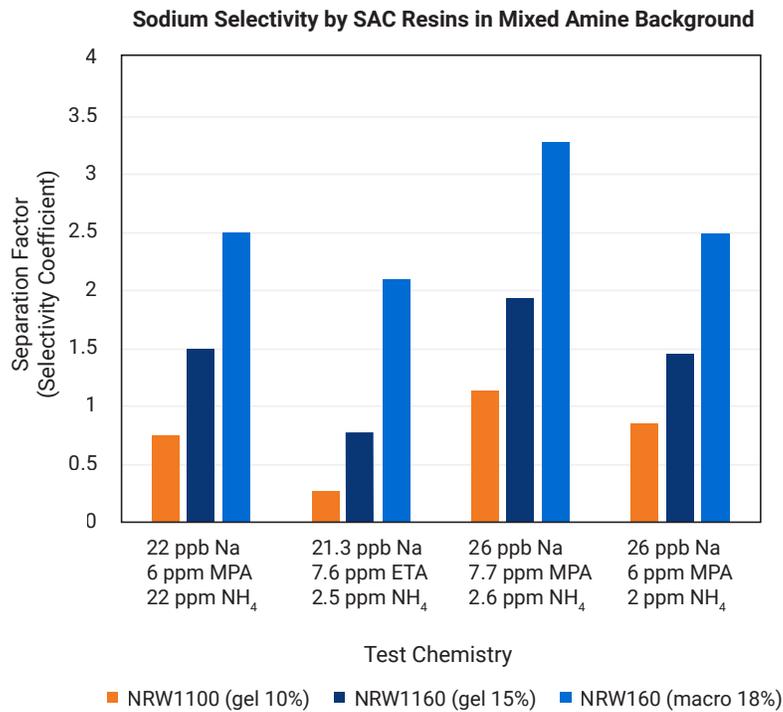


Resin selectivity will change with cross linking, the amine and concentration in solution, and ratio of amine to  $\text{NH}_4^+$ . Figure 2, shows separation factors (selectivity coefficients) for two gel cation resins (NRW1100 and NRW1160) and a macroporous cation (NRW160). Selectivity is the preference of the resin to hold one ion species over another; in this case, the ability to hold  $\text{Na}^+$  verses amine. Selectivity is higher for MPA verses ETA for both the macroporous and gel resins. On a macroporous cation  $\text{Na}^+$  in the presences of MPA and ammonia is held 1.7 times greater than that on a 15% gel cation and 2.7 times greater than on a 10% gel SAC. The macroporous NRW160 selectivity for  $\text{Na}^+$  in an ETA background is 3 times greater than a 15% gel and 5.6 times greater than a 10% gel SAC.

Therefore the macroporous cation will result in lower sodium excursion and more consistent operating life than high capacity gel resins. Studies 5, 7 found similar results but reported greater selectivity for MPA. Additionally reports 2, 5 show  $\text{Na}^+$  leakages from macroporous resin to be lower and more consistent after the amine break than from gel resins.

**FIGURE 2**

**Selectivity of  $\text{Na}^+$   
Comparing Gel and  
Macroporous Cation  
Resins in a Mixed  
Amine Background**

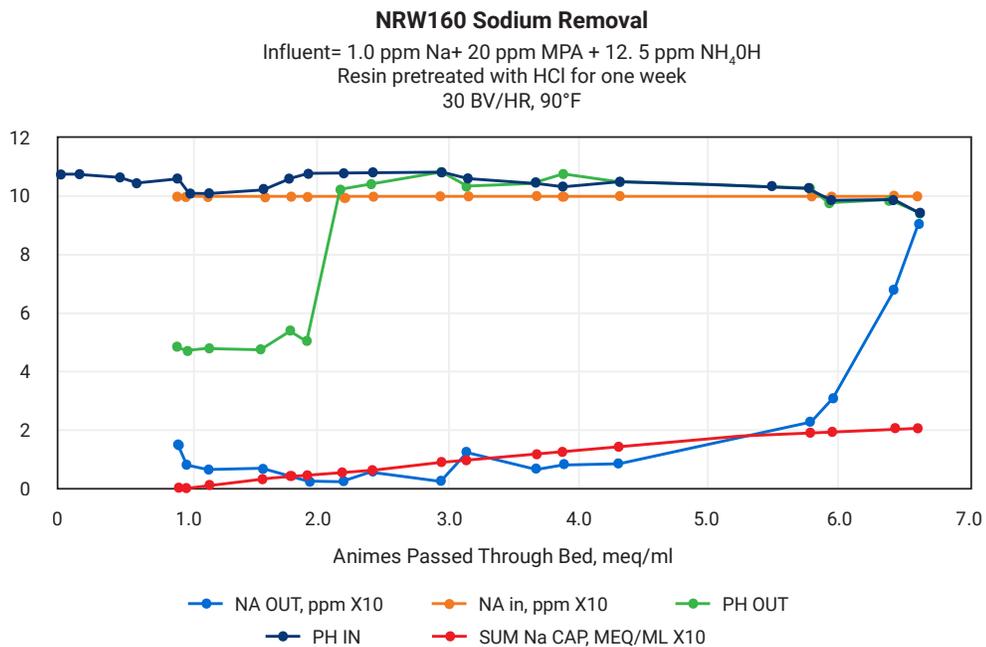


Equilibrium leakage will be from both residual  $\text{Na}^+$  on the resin and  $\text{Na}^+$  entering the bed as represented in Figures 3 and 4 respectively for ETA/ $\text{NH}_4$  and MPA/ $\text{NH}_4$ . Both amines ionize quite differently, with ETA ionizing much more than MPA at pH 10. When both amines were present in a feed at the same equivalent concentrations, the higher fraction of ionized ETA would initially provide greater competition for ion exchanges sites, and would cause greater movement of  $\text{Na}^+$  present on the virgin resin. Factors that impact leakage are service flow, influent ionic chemistry and concentration, resin bed depth, and resin type.

The pKa of ETA and MPA are 7.8 and about 11.6 respectively. At pH 10 this represents about 99% of the ETA is ionized while only about 3% of the MPA is ionized – hence the greater competition experienced with ETA. This falls in line with the leakage of Na<sup>+</sup> being slightly higher at approximately 20% of influent Na<sup>+</sup> (under the specific test conditions) versus approximately 10% for MPA. Operating time of the macroporous cation was found to be nearly 50% longer with the ETA background versus MPA. Na<sup>+</sup> loading was also greater for the ETA. The macroporous cation had 0.2eq of Na/L loaded after 6.5eq of MPA passed through the resin, while 0.34eq of Na/L loaded after 9.5eq ETA passed through the resin. These results are based on artificially higher Na<sup>+</sup> (1ppm) inlet levels due to the inability to monitor Na<sup>+</sup> at sub-ppb levels normally found in the steam generator. This information supports the macroporous cation NRW160 operated in both the ETA and MPA amine form will remove sodium when exhausted in either amine form. Whether the level of removal is sufficient to operate in the amine form will require case by case investigations.

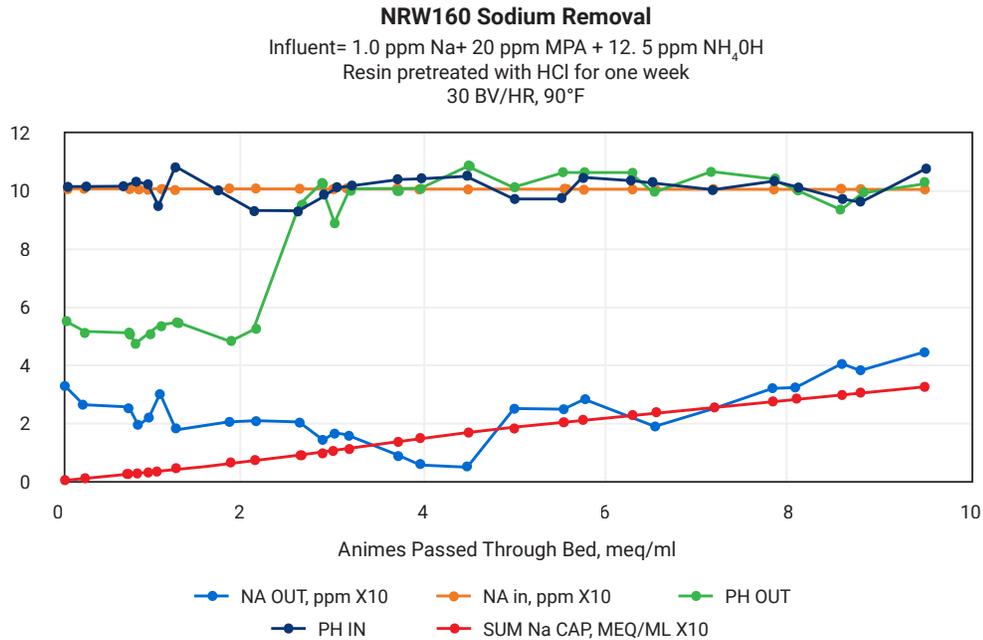
**FIGURE 3**

**MPA Impact  
on Na  
Equilibrium  
Leakage  
Operated at  
1 ppm Na  
Loading**



**FIGURE 4**

**Monoethanol  
Amine Impact  
on Na  
Equilibrium  
Leakage at  
1 ppm Na  
Loading**

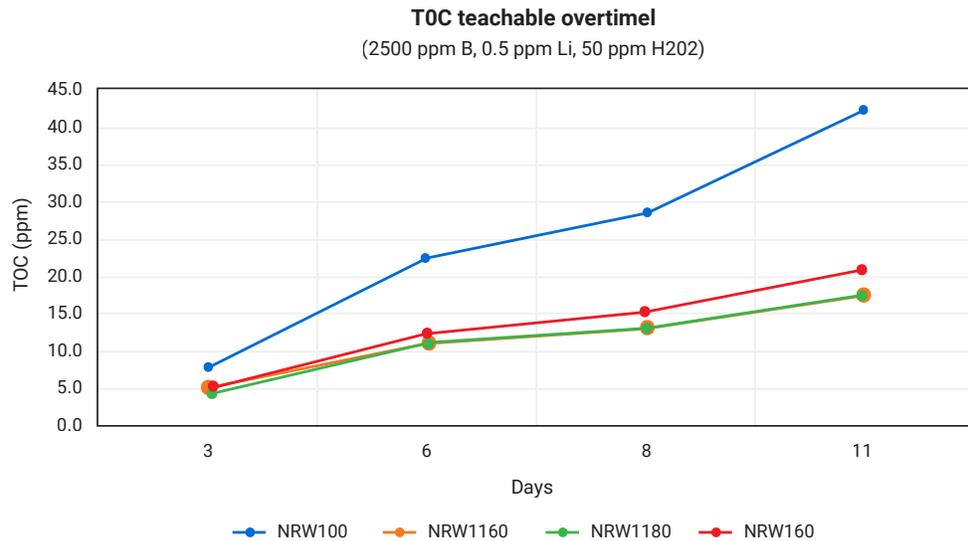


Establishing a specification for Na<sup>+</sup> on SAC resin used for SGBD demineralizers has been suggested at <25ppm dry as resins may be a primary source of Na<sup>+</sup>. When evaluating NRW160 with 10.5ppm Na<sup>+</sup> on a dry weight basis was rinsed with 20ppm ETA solution, the first 10 bed volumes of solution had total of 20ppb of Na<sup>+</sup> which represents approximately 5% of Na<sup>+</sup> remaining on this resin. The second 10 BV had non-detect (<10ppb) Na<sup>+</sup>. When first installing a demineralizer bed rinsing with the blowdown influent for approximately 10 bed volumes will eliminate a small but important volume of sodium from the resin.

Sulfate leakage from macroporous cation resin<sup>2</sup> in the presences of ETA and MPA may require further investigation. However leachable organics from NRW160 when tested in presence of elevated peroxide found TOC to be similar to that of high cross linked gel products (Figure 5). Additionally, when NRW160 was rinsed with 20ppm ETA and there was no detectable (<0.7ppb) sulfate in the first 20 BV's of effluent. Additionally when this solution was UV oxidized no measurable organic sulfate or organic chloride was detected. Therefore sulfate release should not be an issue from this virgin macroporous cation resin.

**FIGURE 5**

**TOC Leachable From NRW160 Over Time in an Elevated Peroxide Solution**



## Conclusion

1. Operating SGBD demineralizers with a macroporous cation NRW160 will result in lower sodium leakage in an amine environment than what will be achieved with gel cation resins.
2. Operating SGBD demineralizer resin in an ETA and MPA amine environment to a sodium break should be possible even when combined with a small amount of ammonia.
3. Factors impacting cation resin performance: a. Selectivity or resin holding ability in a competitive ion background b. Equilibrium leakage or ability of ions to move off the resin c. Kinetic leakage or ions ability to move onto the resin.
4. Plants operating to a sodium break with MPA will see lower sodium leakage while plants with ETA may have approximately double sodium due to equilibrium leakage
5. Resin bed in an ETA environment may operate approximately 50% longer compared to an MPA environment.
6. Systems with in-leakage may be limited to H/OH service.
7. Resins supplied with low level sodium on the cation will minimize sodium being added to the system.
8. The Macroporous cation resin NRW160 when rinsed with an ETA solution had no detectable release of organic or inorganic sulfates.

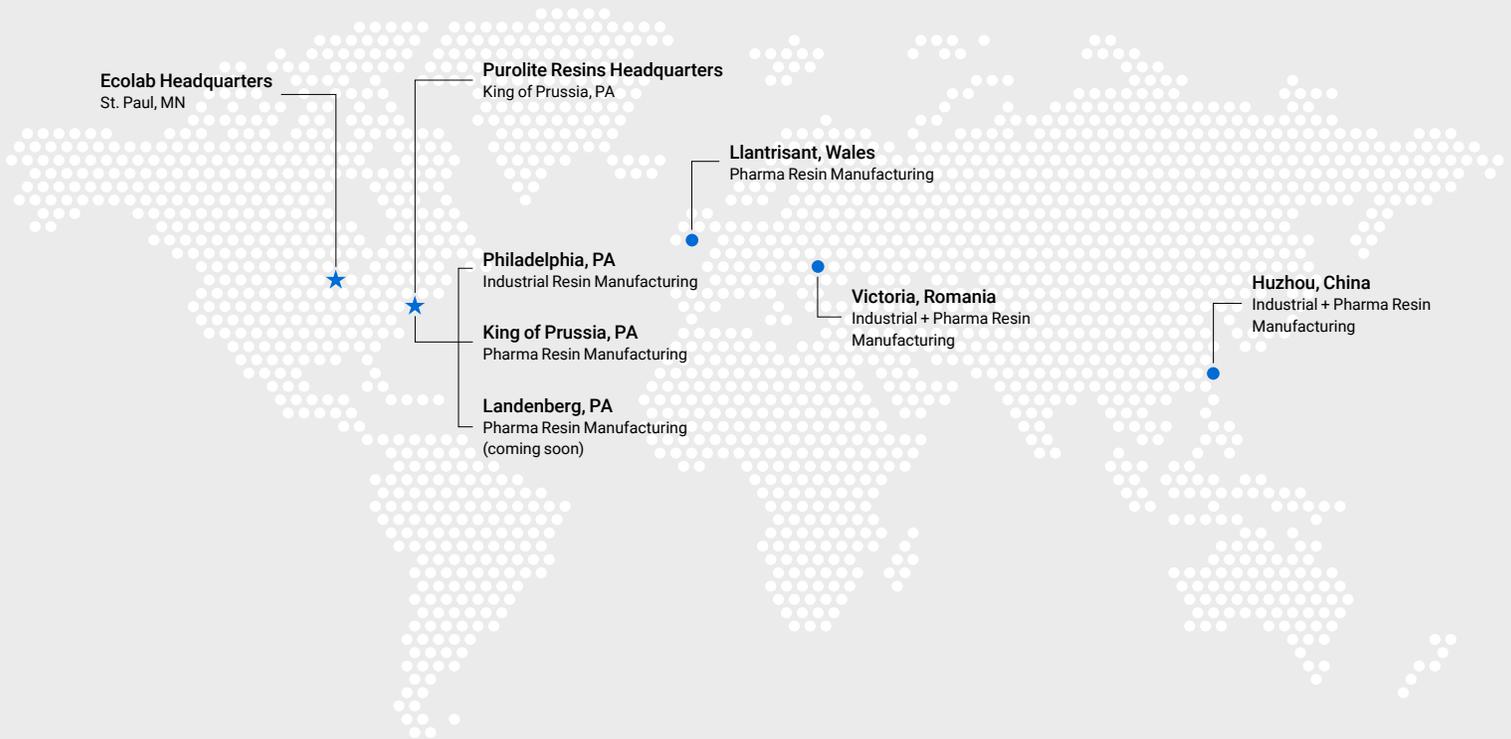
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