THE OXIDATION RESISTANCE OF CATION EXCHANGE RESINS

J.A.Dale and J.Irving, Purolite International Ltd., Pontyclun,
Mid Glamorgan CF72 8YL, UK

1 Introduction

A number of properties of cation exchange resins related to oxidation will be discussed. In particular a novel ion exchage resin has been developed with one particular property of considerable interest. Ion Exchange Resins with resistance to strong oxidising agents has been a major objective for many years. Poor resistance has influenced the performance of synthetic ion exchange resins since their inception. This problem has been addressed regularly over the years. The influences on the rate of oxidation are complex, and many of the factors which affect the resin structure and the functional groups have been clarified.

2 Review of Oxidation Resistance

Some improvement in oxidation resistance was obtained with higher crosslinked cation resins, which can withstand attack for a longer period before their performance suffers significantly.

Resins with modified matrices[1] have been proposed with partial success. These generally are effective for a limited period because the oxidising agent attacks the modified group rather than the polymer backbone. Success is limited : eventually the sacrificial groups are used up and the oxidation reverts, to that of the unmodified resin matrix.

Resins with good oxidation resistance can also suffer other disadvantages. For instance, a more highly crosslinked resin shows slower diffusion during exchange, and is generally more difficult to regenerate. It is also more prone to fouling with high molecular weight organics and also with multivalent ions. It has been shown[2] that hydrated ions such as hydrogen, and hydroxide, have to shed hydration shells to be accomodated in highly crosslinked resins. The resulting increase in charge density allows these aggressive ions to attack the functional group causing less thermaly stability. Hence, the extended life obtained from increased oxidation resistance may be curtailed by some other factors.

3 Mechanisms of Oxidative Attack

The chemistry of oxidative attack is now well known[3,4]. Many papers[5,6,] have shown that the mechanisms can be complex. Hydrogen peroxide, ozone, free chlorine, hypochlorite, chlorine dioxide, chromic, nitric, and peracetic acids, have been studied by a number of workers; all cause resin degradation, especially in the presence of catalysts: UV light, radiation, transition metals. To a lesser extent atmospheric oxygen, and chlorate also cause problems, particularly at higher temperatures.

Hydrogen peroxide is very useful for such studies. Firstly it does not add anything other than oxygen to the structure (unlike chlorine or hypochlorite which can chlorinate the matrix, or chromate which may become irreversibly bound to the resin). Secondly, it is fairly easily handled. Nitric acid on the other hand can produce run-away exotherms.

One of the most important variables affecting the rate of degradation is the presence of transition metals on the resin or in solution. Of these, iron is by far the most important [4,5,6]: firstly because it acts to catalyse the decomposition of hydroperoxides. It is also ubiquitous; and can be expected to be present in any normal ion exchange process, unless special effort is made to remove it. The elimination of iron from systems with hydrogen peroxide or atmospheric oxygen can reduce degradation by orders of magnitude. Copper is also important but less powerful and less common. Alll tests on oxidation resistance need to be carried-out at controlled metal concentrations. Concentrations of the hydrogen peroxide oxidant, temperature and time. need to be specified.

Other variables need to be eliminated or controlled:

3.1 UV light (including daylight) in presence of air (oxygen)

3.2 Radiation

3.3 Resin pH - resins in H^+ form being as a rule more readily oxidised as a rule.

In industrial applications these conditions have to be taken into consideration when discussing the operating performance of a resin and/or equipment. The presence of oxygen in condensate polishing has been shown to be detrimental to thermal stability[7]. For this reason hydrazine has historically been used. More recently, health hazards associated with hydrazine together with changes in materials of construction and the water conditioning chemistry have prompted some industrial power plants to operate oxygenated systems. The full effects on consequent oxidative degradation still have to be evaluated.

Chromium/chromate can act both in a redox/oxidation mode by a subtley different mechanism in which the oxidation is self catalysing, so it is useful to compare this oxidation process also.

4 Influence on Operating Performance

Increased moisture retention gives rise to many problems: loss of physical strength, irreversible resin swelling causing impaction, increased mechanical stress, channelling, and poor distribution of regenerant. Any or all of these can result in severe resin physical breakdown. Removal of the excess resin produced by the irreversible expansion may be necessary. This reduces the capacity of the resin bed (fewer active groups). Also changes in resin selectivity, can produce a lower throughput because of increased leakage/premature end-point.

Linear polymer leachables can foul resin beds down- stream[8,9]. This is particularly important in the operation of mixed beds[10-13]. The effect of carboxylic groups on rinse performance is well known, as is the effect of low molecular weight polyamines (possible degradation products of anion resins) on the kinetics of cation resins[14,15]. An oxidatively resistant resin would have marked advantages in ultra-pure water production.

The ultra-pure water industry is ever mindful of any impurities in the system, particularly TOC, which can effect the quality of production e.g. silicon chips. As the techniques for determination of TOC, have improved, so the full effects of trace leachables have been clearly recognised. Leachables also act as nutrients for bacteria and algae. Regrettably, oxidising agents are the best means of controlling biological growth. Ozone and UV light are frequently used as part of the integrated and complex system needed for Ultra-pure water. Incidences of both ozone and UV light causing resin degradation are well known.

5 New Developments

Purolite International Ltd. has developed a new cation exchange resin type which is truly oxidation resistant. Comparison with the previous modifications, which showed certain advances over conventional more highly crosslinked strong acid cation resins, is dramatic. The resin structure may undergo oxidation, but the performance behaviour itself shows little degradation (criteria 1-6 given below), A standard oxidation test, using specific amounts of 1% hydrogen peroxide and iron at 40°C are strikingly different from previous resins. This is reflected in the study of other properties.

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5.1 Changes in moisture content: are relatively small. Table 1 compares the moisture retention before and after oxidation of the new product, D2908 with a number of standard cation resins including a modified product with partial resistance. All these are severely degraded, without exception. (See Fig.1).

5.2 Increase in polymer leachables: A second property of importance is the release of polymer leachables. When resins are new, they may be specially cleaned so as to reduce the leachables to a minimum. A number of tests have been developed to evaluate this property. Among these is the DIN Standard 54 411 from Germany where Demineralised water is percolated through the resin for periods up to seven days. The TOC (Total Organic Carbon) released is measured. The problem arises that such trace leachables are continually increasing as resin is stored. Among other factors resins are slowly degraded in the presence of oxygen and iron catalyst. A comparison of such degradation following the DIN Test shows that TOC release is negligable when compared with standard resins. (see Table 2)

5,3 The products have extremely high breaking weights. Table 3 gives a comparison of breaking weights before and after oxidation.

Table 1 *Oxidation Resistance Using 1% w/v Hydrogen Peroxide*

Temperature	40°C		Moisture %			
Iron Content	500ppm	Days				
RESIN		0	1	2	3	5
D2908 H form	VALUE:	**56.9**	**57.4**	**58.6**	**60.2**	**65.5**
	NETT D:		0.5	1.7	3.3	8.6
5%DVB SP	VALUE:	**65.1**	**74.3**	**92.9**	sample	
	NETT D:		9.2	27.8		
8%DVB Gel H form	VALUE:	**56.3**	**62.2**	**70.0**	**80.1**	sample
	NETT D:		5.9	13.7	23.8	dissolved
8%DVB Gel Na form	VALUE:	**49.6**	**73.3**	**90.4**	sample	
	NETT D:		23.7	40.8		
8%DVB MP	VALUE:	**64.5**	**68.2**	**75.4**	**92.9**	-
	NETT D:		3.7	10.9	28.4	
12%DVB MP	VALUE:	**55.9**	**58.2**	**60.5**	**70.0**	-
	NETT D:		2.3	4.6	14.1	

Table 2 *Polymer Leachables*

RESIN	BEFORE ppm	AFTER ppm
D2908	3.2	2.9
8%DVB GEL H FORM	2.9	> 100

After 24 Hour Oxidation Test
48 Hour TOC Test

Table 3 *Breaking Weights*

RESIN	BEFORE g	AFTER g
D2908	1184	946
8%DVB GEL H FORM	600	300

After 24 Hour Oxidation Test

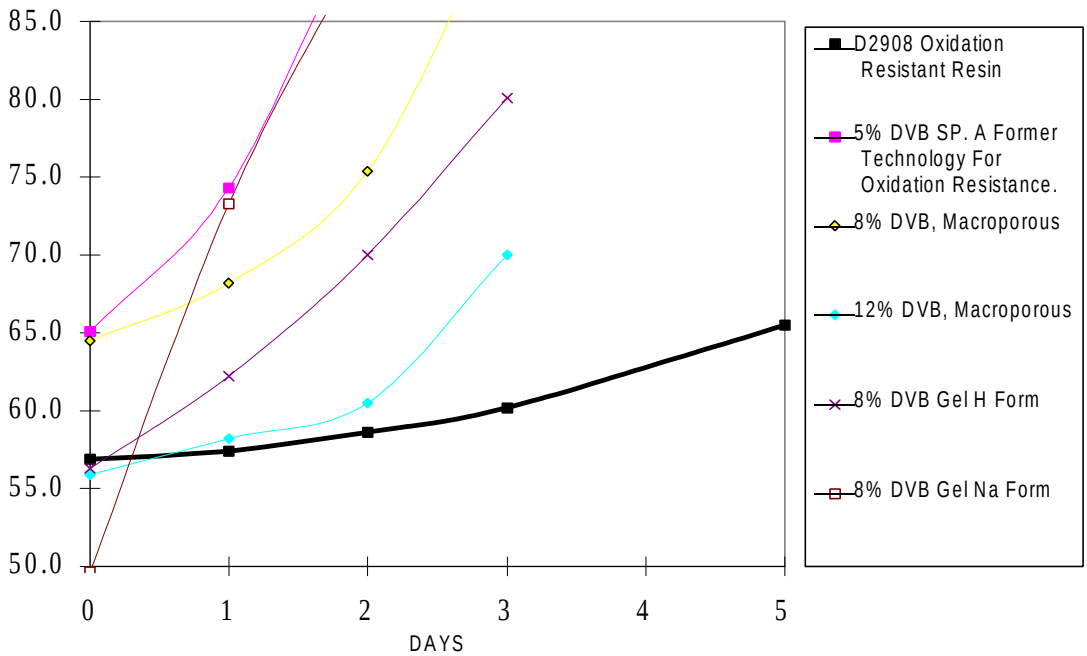


Figure 1 *Oxidation Resistance Tests - Change iIn % Moisture*

5.4 Extent of oxidation. It is evident that the oxidation itself cannot be obviated. Also, the new material is not precisely comparible with conventional resins which lose up to 10% of their mass for an increase in moisture of 10%. Many of the carboxylic groups generated are lost in the leachables whereas the new structure is essentially intact, and the products of oxidation are retained, bound to the resin structure.

` ***5.5 Loss of functional groups:*** When considering cation resins, the loss of functional groups is more or less pro-rata with loss in resin mass, so point 5.4 applies.

5.6 Resin selectivity : both values and trends differ from those of conventional resin. The effect of oxidation has been investigated for sodium/hydrogen exchange only. (See Fig.2.and 3/after)

Oxidation with chromic Acid

A second test using 5% w/v chromic acid/10% sulphuric acid mixture at 90°C was also briefly investigated. The dramatic difference between the conventional resin and the new resin was evident for this oxidative medium also. The results are given in Table 4.

Table 4 *Oxidation Resistance In 5% Chromic Acid*

TEMPERATURE : 90°C		D2908		8% X-	
		Before	After	Before	After
% Moisture	%	57.4	60.5	54.8	sample
Difference			3.1		dissolved
% Dry Matter	%	42.6	39.5	45.2	0.00

Mass (4g Orig Dry Wt)	g	9.39	8.97	8.85	sample
Mass Change	g		-0.42		dissolved
Mass Change	%		-4.47		
Mass Dry Matter	g	4.00	3.54	4.00	0.00
Mass Dry Matter Change	g		-0.46		-
Mass Dry Matter Change	%		-11.42		-

6 Resin Selectivity

Resin selectivity was determined essentially by the technique outlined by Gregor[16], Bonner and Smith[17] using concepts and notation developed later by Anderson [18].

20 mL samples of resin were equilibrated with solutions containing various mole fractions of ion pairs. The resins were then analysed to determine the fraction of each ion loaded.

The resin loading data was then used to plot comparative selectivity curves Fig 2-5. Fig.2 gives a selectivity comparison of fresh resins with the oxidised counterparts. It is most interesting that oxidation changes selectivity in the opposite direction to that for standard resin: as it degrades it behaves like a more highly crosslinked material.

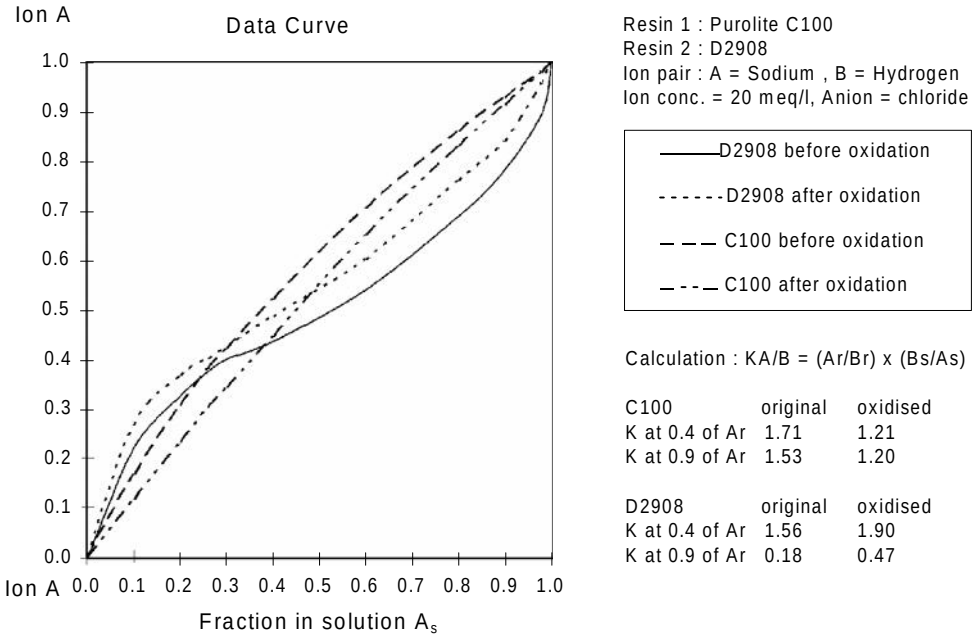


Figure 2 *Comparison Of Sodium/Hydrogen Selectivity, .*

The data for sodium/hydrogen exchange compares D2908 with Purolite C-100, for chloride anion (Fig.2) and sulphate (Fig.3). Both resins are marginally more selective for sodium where the co-ion is sulphate. Purolite C-100 was in line with 8% crosslinked resins given in Helferich "Ion Exchange"[19].

The new oxidation resistant resin, shows considerable differences in selectivity. Where the fraction of sodium is < 0.25 in solution the novel resin has higher selectivity for sodium; above this level the selectivity is significantly lower. In certain situations this difference may offer significant advantages. It is more difficult to predict kinetic and fouling behaviour, but the fact that the sites have the selectivity of a more easily-regenerated or easily-cleaned, lower crosslinked resin, offers considerable incentive to study these. The combination of high selectivity for a limited number of sites, together with a tough oxidation resistant structure which does not produce leachables as a result of oxidative breakdown makes this resin potentially useful for condensate polishing where iron levels build up to produce an oxidation prone environment.

For treatment of condensate, sodium/ammonia selectivity was studied. (see Fig.4). Again the data for Purolite C-100 are in line with published values. The data for the new resin are interesting; for a mole fraction high in ammonia, the resin is more selective for sodium. However when using limited amounts of regenerant counterflow, as the fraction of ammonia falls, so the resin becomes more selective for ammonia. This resin may
therefore be used to advantage to remove trace levels of sodium from solution. It would be expected that the higher hydration of hydrogen ion will be kinetically more efficient.

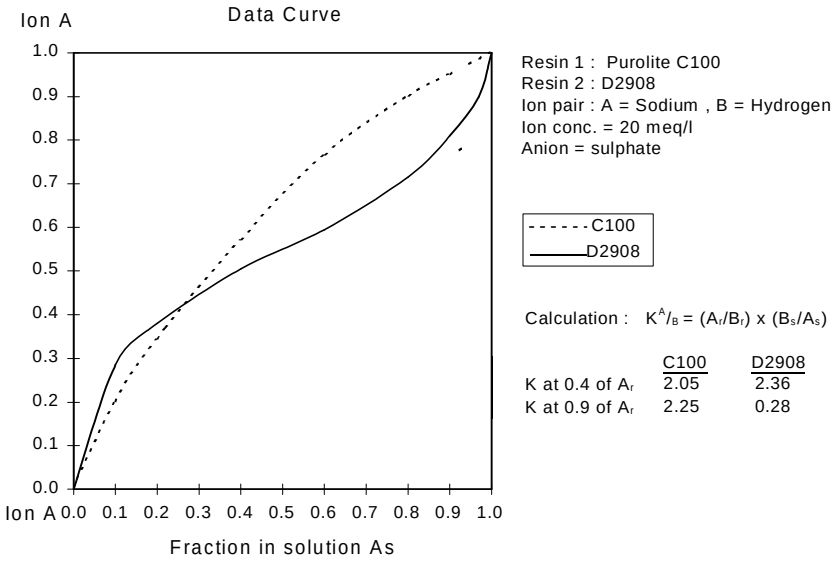


Figure 3 *Sodium / Hydrogen Selectivity (Anion = Sulphate)*

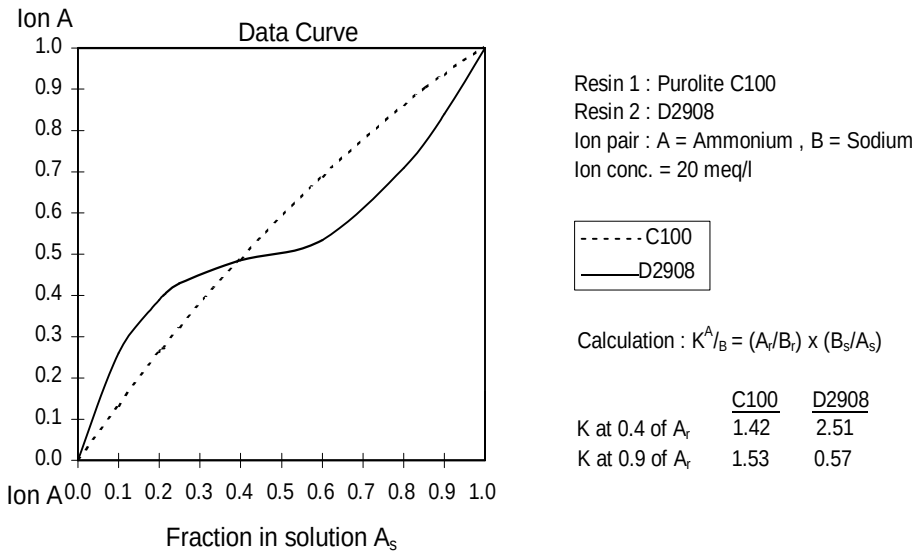
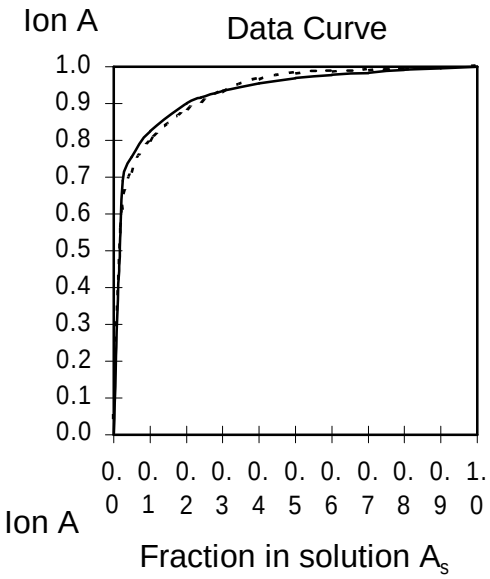


Figure 4 *Ammonium / Sodium Selectivity*

The calcium/sodium equilibria are remarkably similar, Fig.5; However because of concentration differences in the resin phase the numerical values for K vary. It remains to be seen how well the D2908 will perform as a softening resin. In any case, the resin is unlikely to be cost effective for most softening applications.



Resin 1 : Purolite C100
Resin 2 : D2908
Ion pair : A = Calcium , B = Sodium
Ion conc. = 20 meq/l
Anion = chloride

------C100
———D2908

Calculation :
$K^A/_B = (A_r/B_r^2)x(B_s^2/A_s)x(C_s/C_r)$
where A = divalent anion

	C100	D2908
K at 0.4 of A_r	0.90	1.94
K at 0.9 of A_r	2.17	6.70

Figure 5 *Calcium / Sodium Selectivity*

7 Thermal Stability

The thermal properties of this novel material are currently being evaluated. It is well known that cation resins are more thermally stable than anion resins. However the principles put forward by Chew, Whitney and Diamond,[2] together with the studies by Fisher[9] and Auerswald[10] would indicate that the thermal breakdown mechanism is the same. Namely that the agressive hydrogen ion (to be compared with the hydroxide ion in anion resins) attacks the bond which links the functional group to the resin matrix. The higher the moisture content, the more hydrated the hydrogen ion and the greater the possibility of a suitable spacial configuration. This produces a lower charge density so reducing the rate of attack. The nature of the novel resin structure would suggest that many of the hydrogen sites are in general more highly hydrated than those in conventional 8% cross-linked resins. This is supported by the selectivity data. The novel resins contain a substantial majority of sites which are less selective for hydrogen ion. Meyers and Boyd[20] showed that the higher the crosslinking the larger the Na/H selectivity coefficient. It follows that the higher the charge density of the hydrogen ion the slower the diffusion and the more relatively selective becomes the resin. The converse therefore should apply. The D2980 has sites with a larger range of selectivities than conventional resins, however the majority of sites are of lower selectivity when compared to an 8% cross-linked resin and

would therefore appear to be more highly hydrated. It follows that the majority of sites should therefore be
more thermally stable.

Table 5 illustrates the results of Thermal Stability Tests carried out at 100°C. This temperature was chosen because it is the maximum temperature at which resins may conveniently used at atmospheric pressure. Hence these initial tests only serve to confirm that the novel resins are no less stable than conventional resins
at temperatures up to 100°C. Operation at higher temperatures presents some minor difficulties in that the containing vessel needs to be pressurised. In addition care has to be taken that the hydrogen form resin cannot corrode any metallic container.

Table 5 *Thermo Stability*

	Moisture %	SAC eq/kg	WAC eq/kg	Total eq/kg
Initial Value @ 20°C	43.2	2.92	0.61	3.53
Stability @ 100°C :				
Without Oxidation / Moderate Iron	44.0	2.67	0.72	3.39
With Oxidation / Low Iron	47.2	3.24	0.62	3.86
With Oxidation / High Iron	49.4	2.80	1.62	4.42

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USA
Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe
Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific
Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com