

Zeolites as Sustainable Alternatives to Traditional Tanning Chemistries

William R. Wise^a, Stefan J. Davis^a, Wouter E. Hendriksen^b, Dirick J. A. Von Behr^b, Sujay Prabakar^c, Yi Zhang^c

^aInstitute for Creative Leather Technologies, The University of Northampton, University Drive, Northampton, NN15PH, United Kingdom

^bSmit & Zoon, Nijverheidslaan 48, 1382LK Weesp, The Netherlands

^cLeather and Shoe Research Association of New Zealand, Palmerston North, New Zealand

Supplementary Material

pH Profile of Zeolites During Acid Hydrolysis and Rebasification

Zeolite equating to 37 mmol of Al(III) was suspended in 100 ml of deionised water. 2.0 ml aliquots of 10% HCl (w/w) were added from a burette and the suspension pH was monitored for 10 minutes using a digital pH meter and probe (Mettler Toledo, SevenMulti, InLab 413 electrode) at 23.0 ± 1.0 °C. The total 10% HCl (w/w) addition was 50 ml, which equated to a $[H^+]:[Al^{3+}]$ molar ratio range of 0.0 – 4.0. After the addition of 4.0 molar equivalents, the suspension was left to hydrolyse under constant agitation for 10 minutes. 2.0 ml aliquots of 10% NaOH (w/w) were then added from a burette and the suspension pH was monitored for the same timeframe. The total 10% NaOH (w/w) addition was 50 ml, which equated to a $[OH^-]:[Al^{3+}]$ molar ratio range of 0.0 – 4.0.

The pH profiles of acid-hydrolysed and rebasified zeolite suspensions are shown in figure S1. Three stages of behaviour: initial pH decrease due to the increase of $[H^+]$ in solution, followed by a plateau stage where increases in $[H^+]$ do not result in a change in system pH, and finally a return to the originally observed behaviour where pH decreases are due to the increase of $[H^+]$ in solution, which agrees with the observations by Cook *et. al.*¹

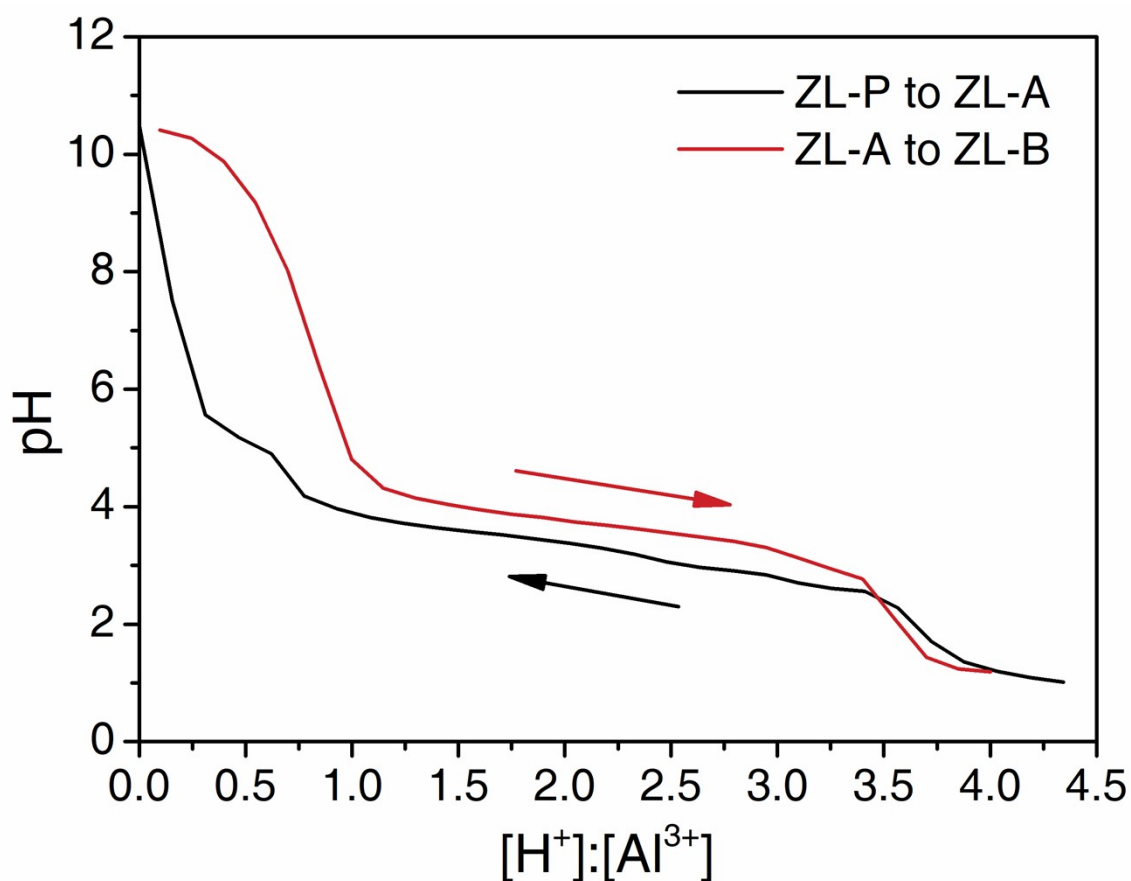
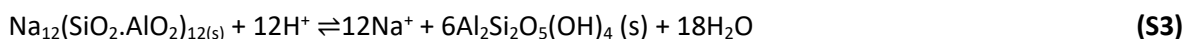
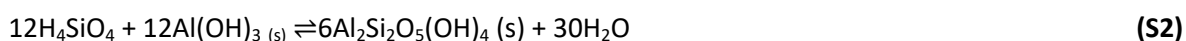
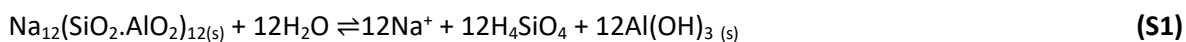


Figure S1: pH vs $[H^+]:[Al^{3+}]$ profiles of zeolite suspensions during acid hydrolysis (red) and re-basification (black).

The acid hydrolysis profile showed a plateau stage spanning 2.5 $[H^+]:[Al^{3+}]$, which is a consequence of the consumption of H^+ during the acid hydrolysis of zeolite.² Considering the relatively large molecular weight of the zeolite network, it is not surprising that comparatively larger quantities of H^+ are required to complete the hydrolysis process. When suspended in water, type A zeolites increase the pH to 10.0 - 10.5 due to the partial hydrolysis and formation of NaOH.³ Ion-exchange with H^+ cannot occur in water without collapse of the crystal structure and in strong acidic media it completely dissolves.^{3,4,5,6} During acid hydrolysis there are two expected mechanisms: at $[H^+]:[Al^{3+}]$ ratios less than 1, H^+ uptake is facilitated by reversible ion-exchange with Na^+ followed by partial hydrolysis, whereas $[H^+]:[Al^{3+}]$ ratios greater than 1, hydrolysis compromises the zeolite structure typically requiring $[H^+]:[Al^{3+}]$ ratios greater than 3 to complete the process.¹ High concentrations of cations, including Na^+ or Ca^{2+} , in solution can impede ion-exchange with H^+ and slow the rate of acid hydrolysis.¹ The presence of chelating agents such as sodium citrate increase the rate of acid consumption during acid hydrolysis due to the complexing agent solubilising the otherwise insoluble aluminium (III) in the degradation products.¹ Hydrolysis and condensation of aluminium (III) and silicon (IV) occur at different rates, suggesting incongruent processes, which are likely to form different aluminosilicate structures upon re-basification.¹ Halloysite, kaolinite, bayerite and gibbsite general structures have

been suggested in the literature.^{7,8,9} Equations S1, S2 and S3, where equation S3 is the sum of equations S1 and S2, describe the hydrolysis of a type A zeolite leading to the formation halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).^{7,8,9} Figure S1 also shows the pH profiles during re-basification with NaOH exhibit same three phases of behaviour, but in the reverse order with a plateau stage spanning approximately 2.6 $[\text{OH}^-]:[\text{Al}^{3+}]$.



Fourier Transform Infrared (FTIR) Spectroscopy Peak Table

Table S1: Peak table for FTIR spectra in figure 1

Peak Number	Peak Wavenumber (cm^{-1})		
	Zeolite (ZL-P)	Dried pickle Filtrate (ZL-A)	Dried activated hydrogel pH 5.5 (ZL-B)
1	1718	1724	1724
2	1692	1699	1702
3	1615	1601	1593
4	-	1469	1466
5	1416	1414	1420
6	-	1334	1349
7	1327	1297	1301
8	1106	1109	1095
9	969	979	990
10	-	917	-
11	-	868	-
12	834	814	814
13	768	-	770
14	662	-	684
15	626	614	611
16	571	571	571

Energy Dispersive X-ray (EDX) line scans

The Energy Dispersive X-ray (EDX) line scans for the cross-sections of zeolite-stabilised bovine hides are listed in figure S2. Figure S2A is a micrograph of zeolite-stabilised bovine collagen (COL-ZB) showing the grain (top), corium (middle) and flesh (bottom). Figure S2B compares the relative variance in Al (red) and Si (blue) from grain (Right) to flesh (left) of the same specimen in a 5-point moving average format. Figure S2C compares the overall average Al and Si through the specimen cross-section and cross-references to pickled (untanned) collagen (COL-UC) and aluminium triformalate-stabilised (COL-ALF)

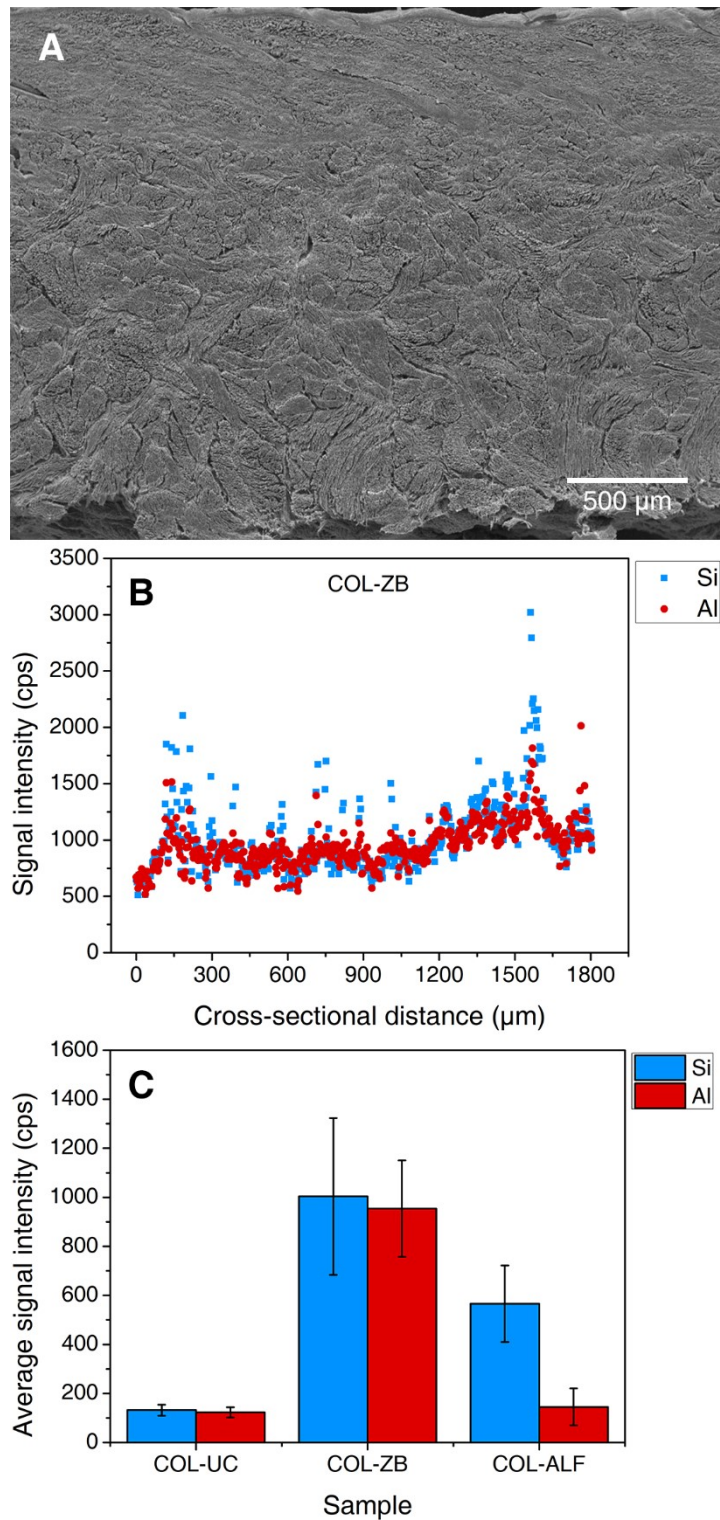


Figure S2: micrograph of zeolite-stabilised bovine collagen (COL-ZB) (A), 5-point moving average EDX overlays vs cross-section of Si (blue) and Al (red) from the flesh (left) to the grain (right) (B), the overall average Al and Si through the specimen cross-referenced to untanned collagen (COL-UC) and aluminium triformate-stabilised (COL-ALF) (C) the area covered is 5.4mm^2

References

- ¹ T. E. Cook, W. A. Cilley, A. C. Savitsky and B. H. Wiers, *Environ. Sci. Technol.*, 1982, **16**, 344
- ² F. Chiardelli, N. Costantini, A.D. Covington *J. Am. Leather Chem. Assoc.*, 2000, **95**, 125
- ³ P. A. Belinskaya, S. P. Zhdanov, E. A. Materova and M. A. Shubaeva, *Theor. Ionnoy Obmena Khromatogr., Tr. Vses. Nauch.-Tekh. Konf.*, 1965, 37
- ⁴ D. P. Roelofsen, E. R. J. Wils and H. Van Bekkum, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1437
- ⁵ C. V. McDaniel, P. K. Maher, *ACS Monogr.*, 1976, **171**, 296
- ⁶ D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974
- ⁷ R. E. York, *Applied Clay Mineralogy*, McGraw-Hill, New York, 1962, 30
- ⁸ W. L. Robert, G. R. Rapp Jr., J. Weber, *Encyclopaedia of Minerals*, Van Nostrand Reinhold Co., New York, 1974
- ⁹ W. D. Hopping, *J. Water pollut. Control Fed.*, 1978, **50**, 433