Role of nanoporosity on metal binding properties of wool powders

Radhika Naik[1], Guiqing Wen[2], M.S. Dharmaprakash[1], Sabrina Hureau[1], Akira. Uedono[3], Peter. G. Cookson[2] and Suzanne. V. Smith[1]

[1]Centre for Anti-matter Matters Studies, ANSTO, Menai, NSW 2234. [2]Institute for Technology Research and Innovation, Deakin University, Geelong, VIC 3217. [3]Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305–8573, Japan

The present study investigates the role of nanoporosity in wool powders on their metal binding properties. Various wool powder forms were produced by milling merino wool, and exposing them to various transition metal ions over a range of pH. Positron annihilation lifetime spectroscopy (PALS) analysis was used to investigate changes in nanoporosity on processing and after exposure to metal ion.

The wool powders were found to rapidly take up the metal ions (15 to 60 minutes). The metal ions such as Co^{2+} and Cu^{2+} could be removed rapidly by exposure to pH 4 solutions. Loading capacity of wool powder was found to be higher (up to 10 fold) compared to commercial ion exchange resins under similar condition (see Figure 1). PALS analysis of wool powders showed that powdering methods did not affect the nanoporosity or metal binding properties of these materials. Collectively the data suggest the basic structural framework of these wool powders are not altered on processing. The wool powders have potential for recovery and recycling of metal ions for environmental and industrial effluents.

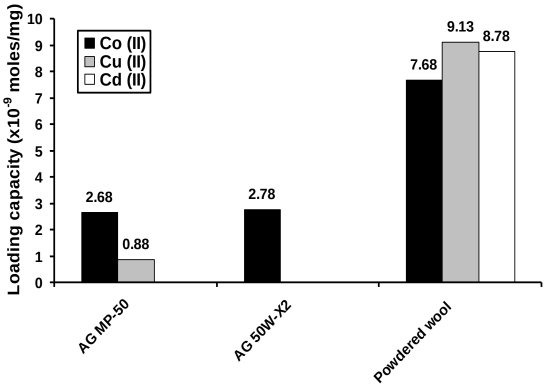

Figure 1. Metal ion loading capacity of wool powders vs commercial ion exchange resins at pH 8.

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Dr. Radhika Naik

radhika.naik@ansto.gov.au

Guiqing Wen, M.S. Dharmaprakash, Sabrina Hureau, Akira. Uedono, Peter. G. Cookson and Suzanne. V. Smith

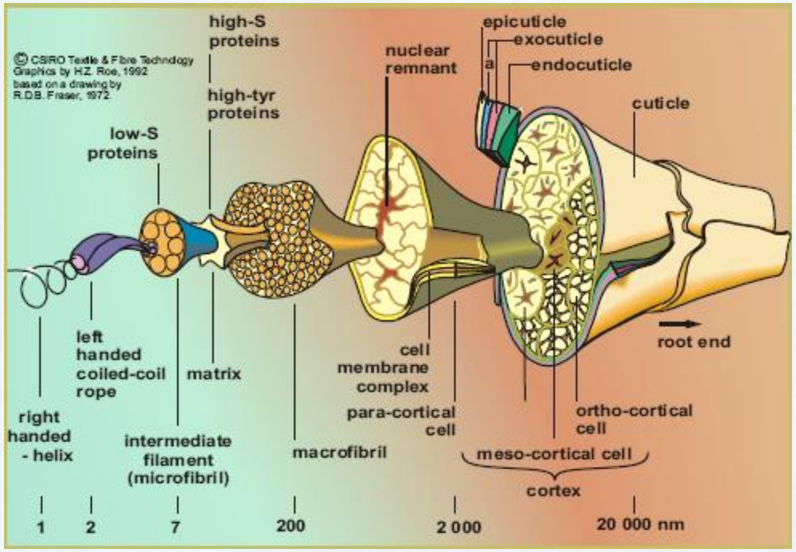
DEAKIN UNIVERSITY

THE UNIVERSITY OF WESTERN AUSTRALIA

筑波大学 University of Tsukuba

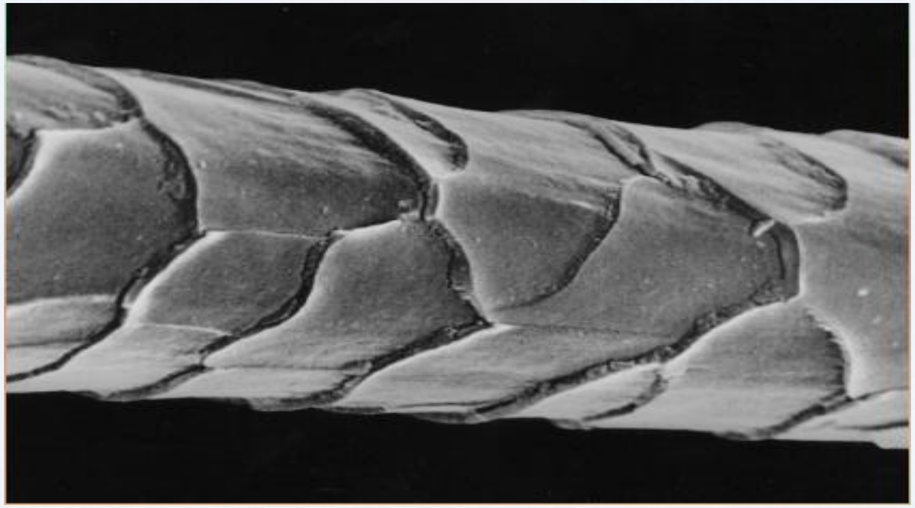
AINSE

Structure of wool



Source: http://www.csiro.au/files/files/p9ti.pdf

- Defined as a biological composite
  - Chemically and physically heterogeneous
  - Complex internal cortex and external cuticle
  - ~90% fibre is cortex



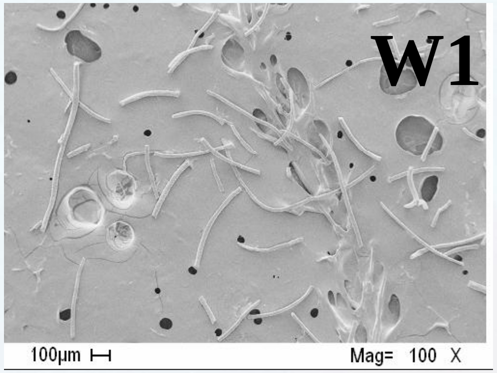
Source: http://www.csiro.au/files/files/p9ti.pdf

- Australian merino wool
  - Fibre diameter 17-25 µm

Production of wool samples

(20.42µm mean diameter)

Chopping →



(~ 500 µm in length)

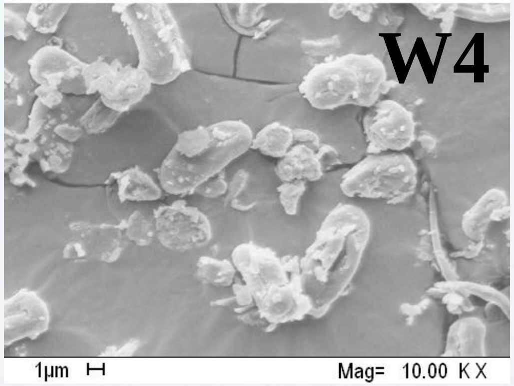
Grinding

(~150 µm in length)

Chemical treatment

dichloroisocyanuric acid
(sodium salt) : 4%
pH 4-4.5, 50 minutes,
room temp.

← **Air-jet milling**

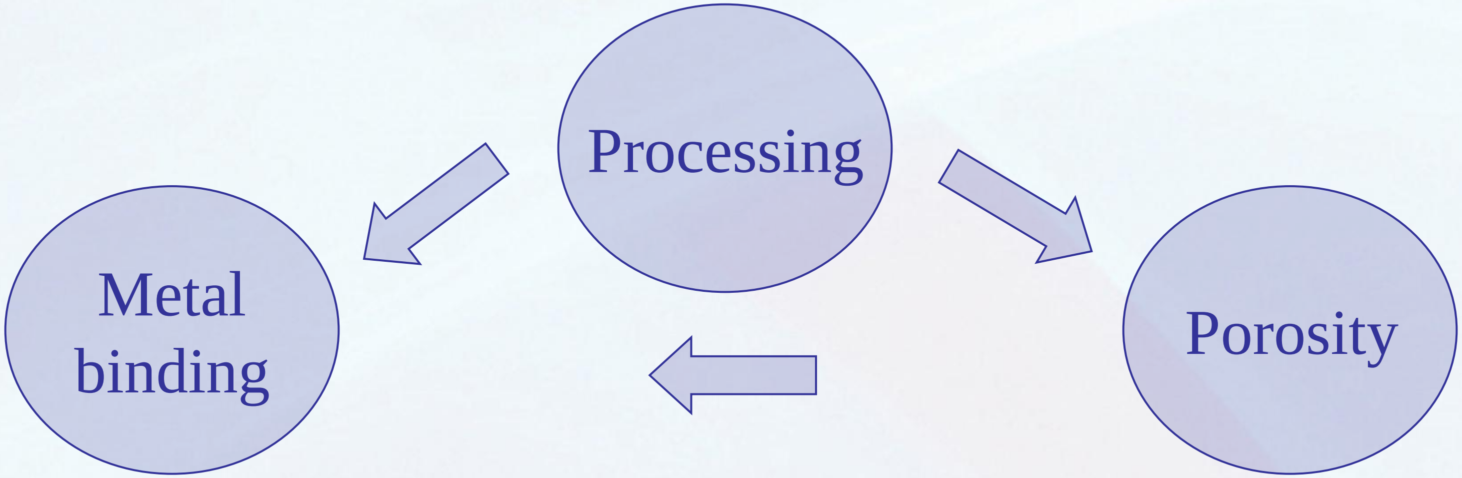


(mean particle size: 4.6 µm)

Particle size = Median of volume based particle size distribution

-- *Powder Technology 193 (2009) 200-207*

Aim



- Co^{2+}, Cu^{2+}, Cd^{2+}
- Effect of pH
- Rate of uptake
- Loading capacity
- Radiotracer

- SEM (Scanning elelctron microprobe)

  >50nm (macropore)
- BET (Brunauer, Emmett, Teller) gas absorption

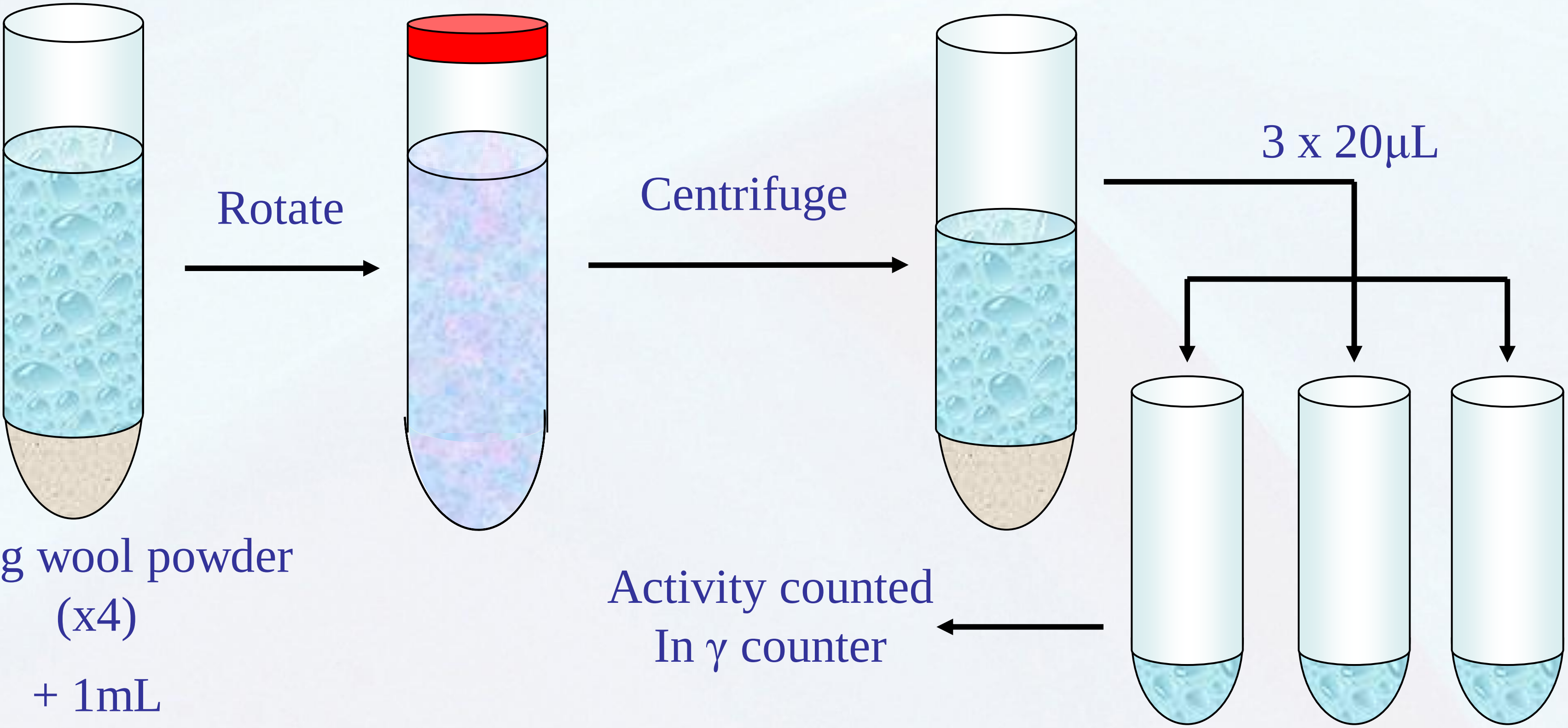
  10-50nm (mesopore)
- PALS (Positron annihilation lifetime spectroscopy)

  0.1-10nm (micropore)

Metal binding: Experimental conditions

- $^{57}Co^{2+}/Co^{2+}$, $^{64}Cu^{2+}/Cu^{2+}$, $^{109}Cd^{2+}/Cd^{2+}$
- pH: 3 to 9
- Temperature: 23°C
- $[M^{2+}] = 10^{-3}$ to 10^{-6}M

Metal binding: Experimental procedure



Rotate

Centrifuge

3 x 20µL

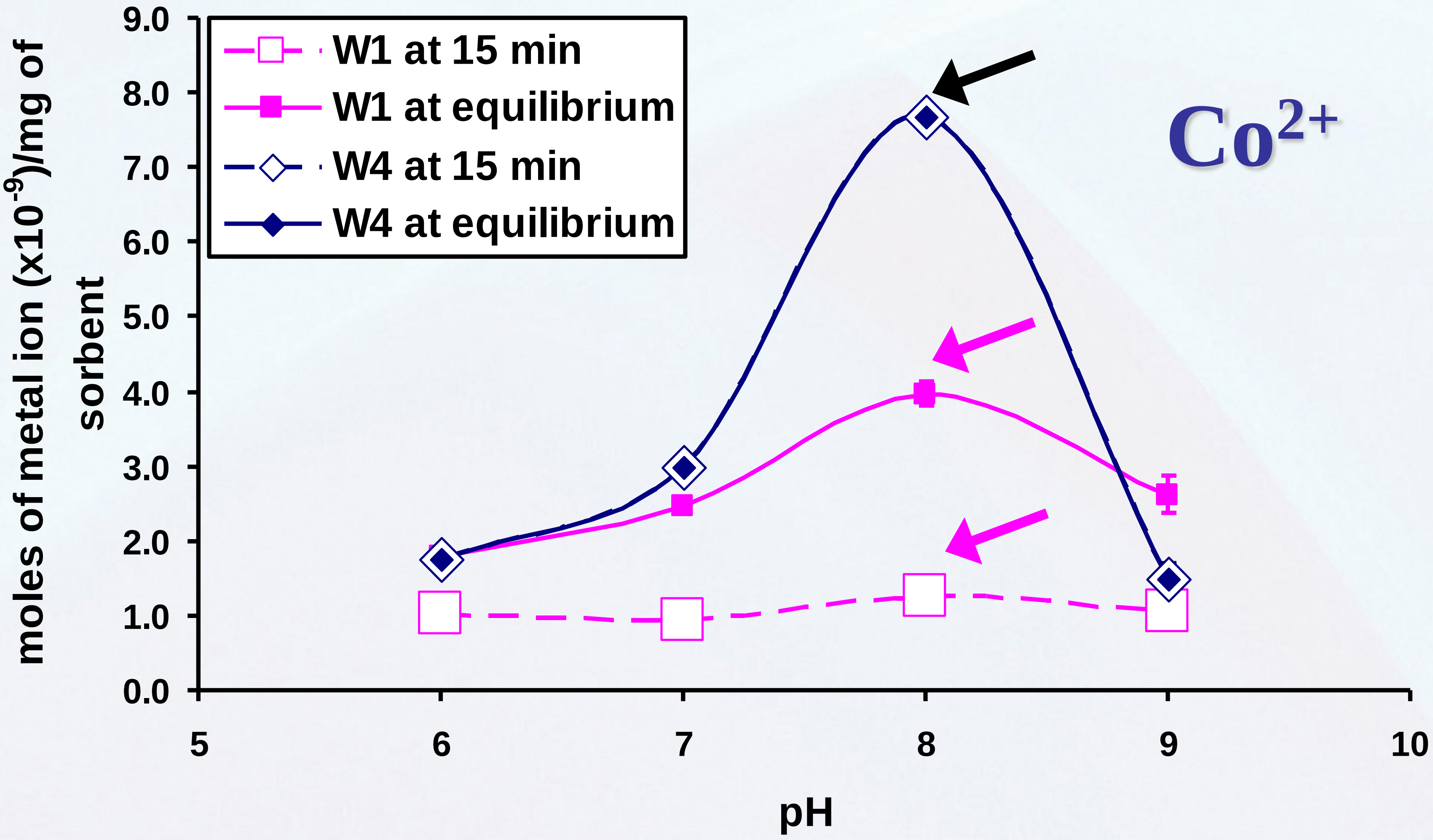
Activity counted
In γ counter

~10mg wool powder
(x4)

+ 1mL
(metal ion +
radiometal ion +
buffer)

- Fast (10 sec), sensitive (10^{-3} ppb)
- Small volume (µL)
- High throughput (~800 readings)
- Independent of reaction media

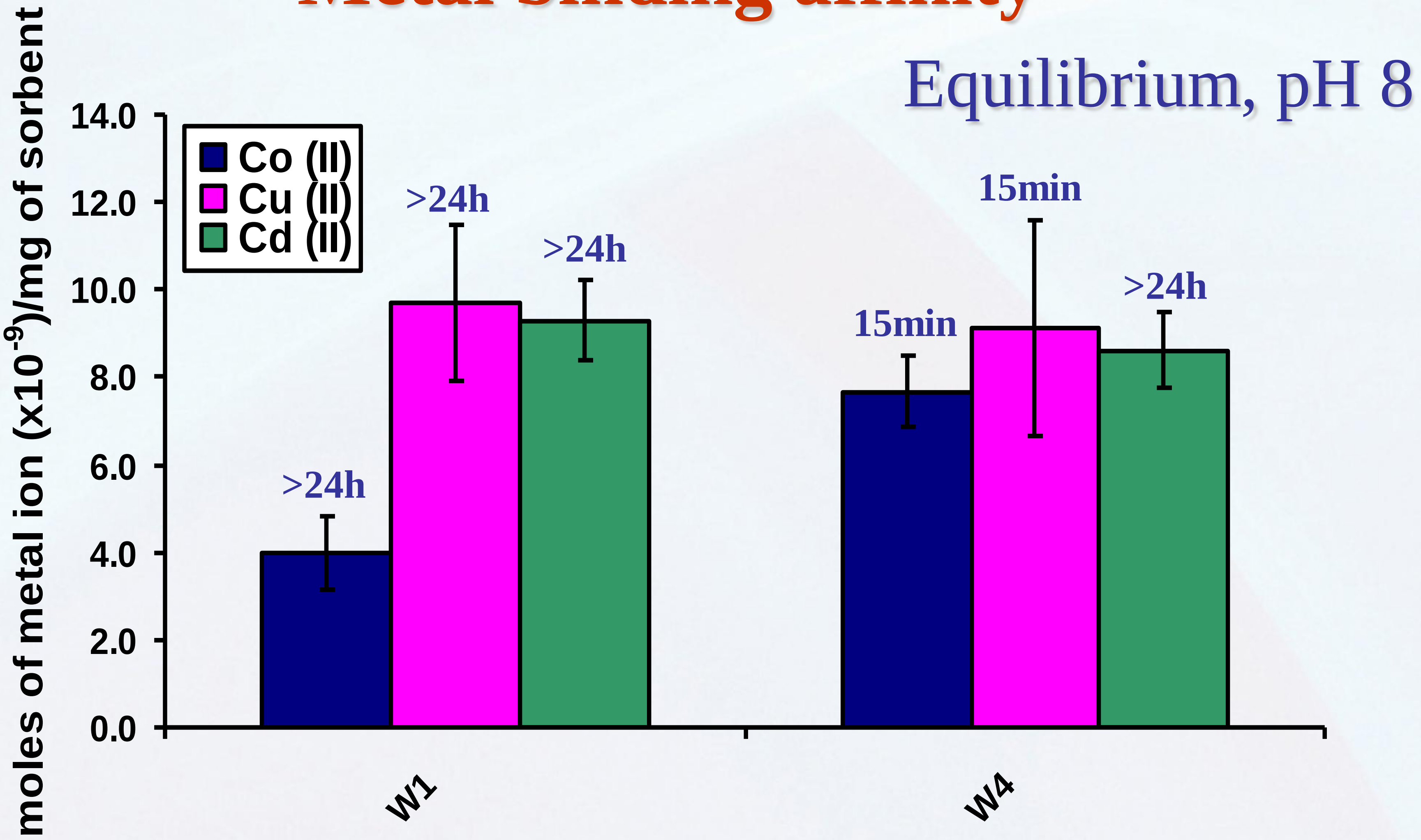
Metal Binding: Effect of processing and pH



Co^{2+}

$[M^{2+}] = 10^{-4}$M; powder 10 mg; Temp.23°C; Total Vol: 1.0 mL; centrifuge; 5000 rpm; n=12

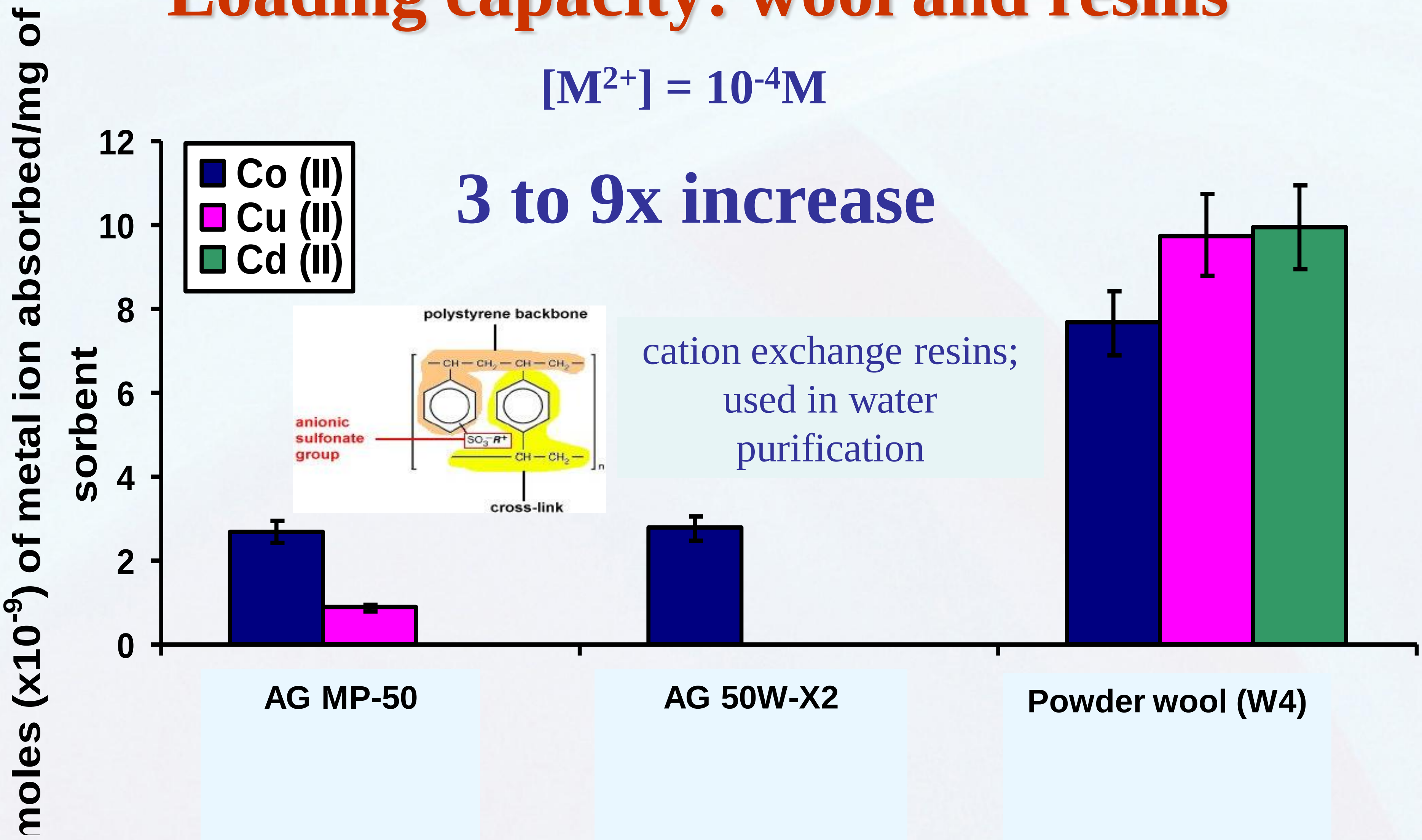
Metal binding affinity



[M^{2+}] = 10^{-4}M; powder 10 mg; Temp.23°C; Total Vol: 1.0 mL; centrifuge; 5000 rpm; n=12

Loading capacity: wool and resins

$[M^{2+}] = 10^{-4}M$

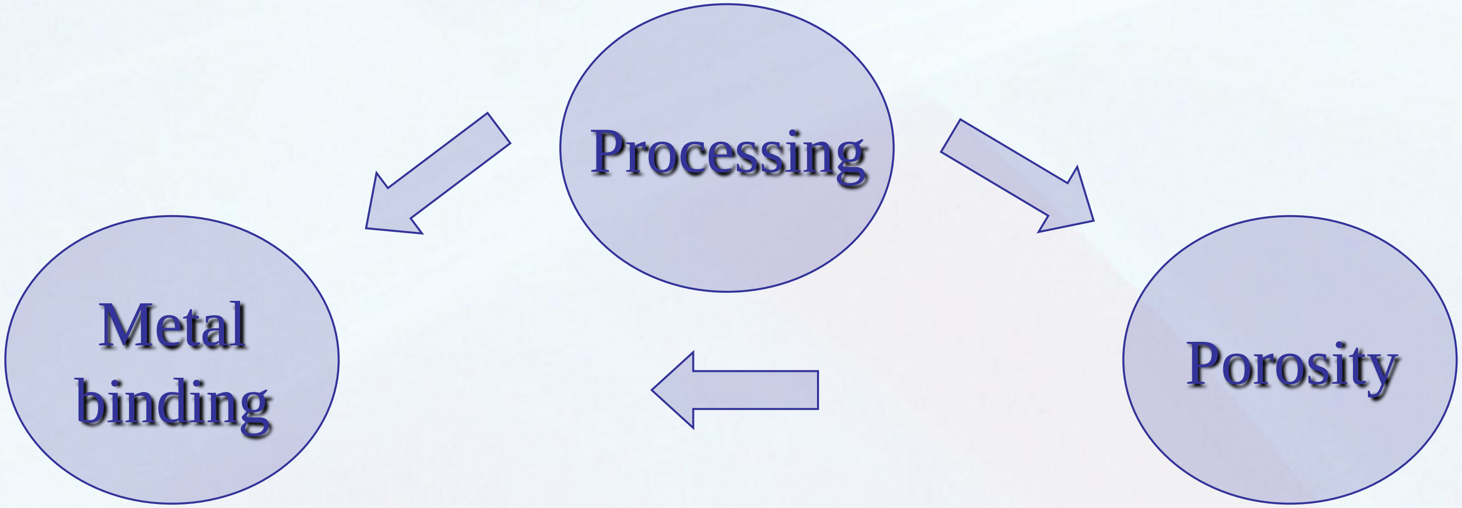


3 to 9x increase

cation exchange resins; used in water purification

powder 10 mg; Temp.23°C; Total Vol: 1.0 mL; centrifuge; 5000 rpm

Aim



- ➢ Co^{2+}, Cu^{2+}, Cd^{2+}
- ➢ Effect of pH
- ➢ Rate of uptake
- ➢ Loading capacity
- ➢ Radiotracer

➢ SEM (Scanning elelctron microprobe)
>50nm (macropore)

➢ BET (Brunauer, Emmett, Teller) gas absorption

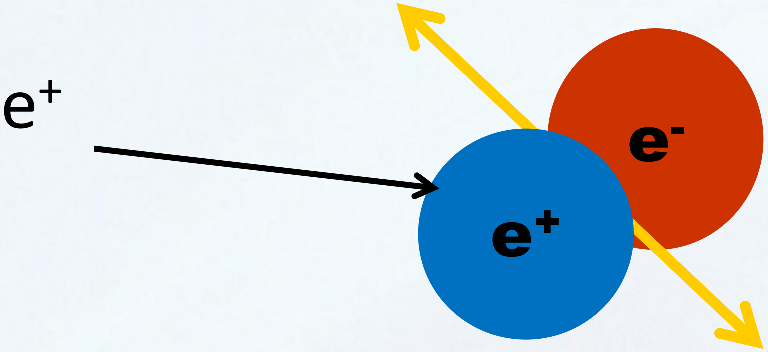
10-50nm (mesopore)

➢ PALS (Positron annihilation lifetime spectroscopy)

0.1-10nm (micropore)

PALS

(Positron annihilation lifetime spectroscopy)

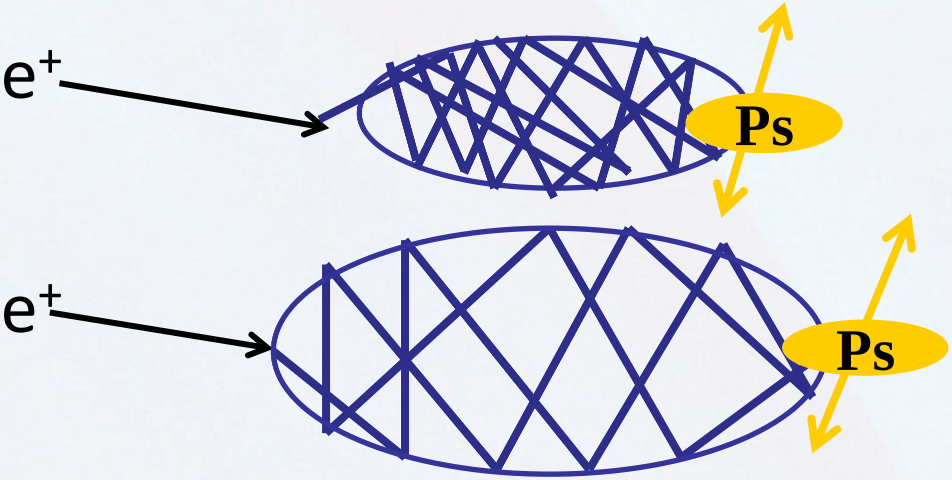


Positronium (Ps):

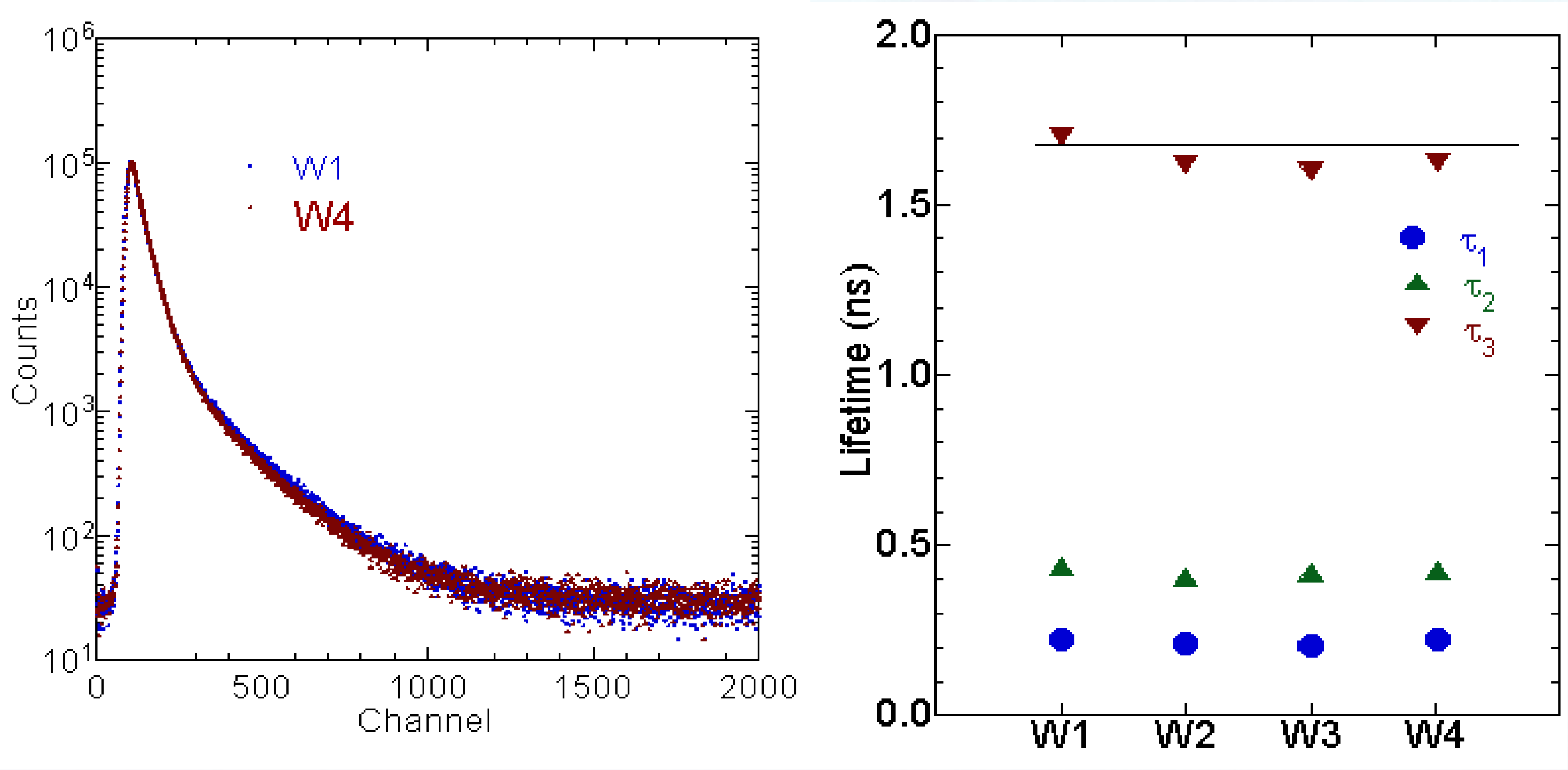
- para-Ps (singlet, short-lived)
- ortho-Ps (triplet, longer-lived)
- Probability of formation p:o is 1:3

- Positron lifetime (τ) is a function of the electron density in the material

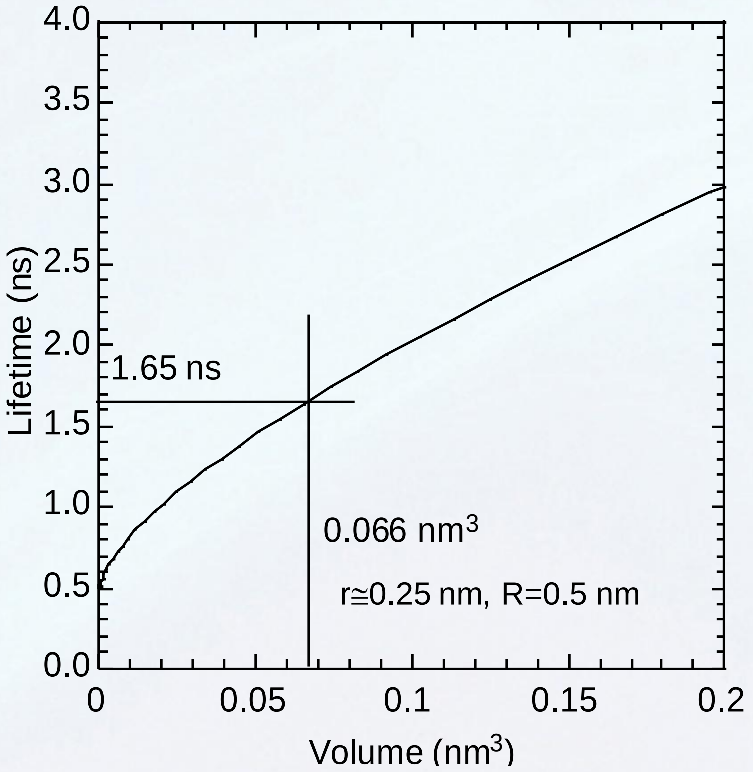
- Longer lifetime indicates larger pore volume



Porosity: Effect of processing



Porosity: Effect of processing



Wool sample	Pore size (nm)
W1	0.517
W4	0.521

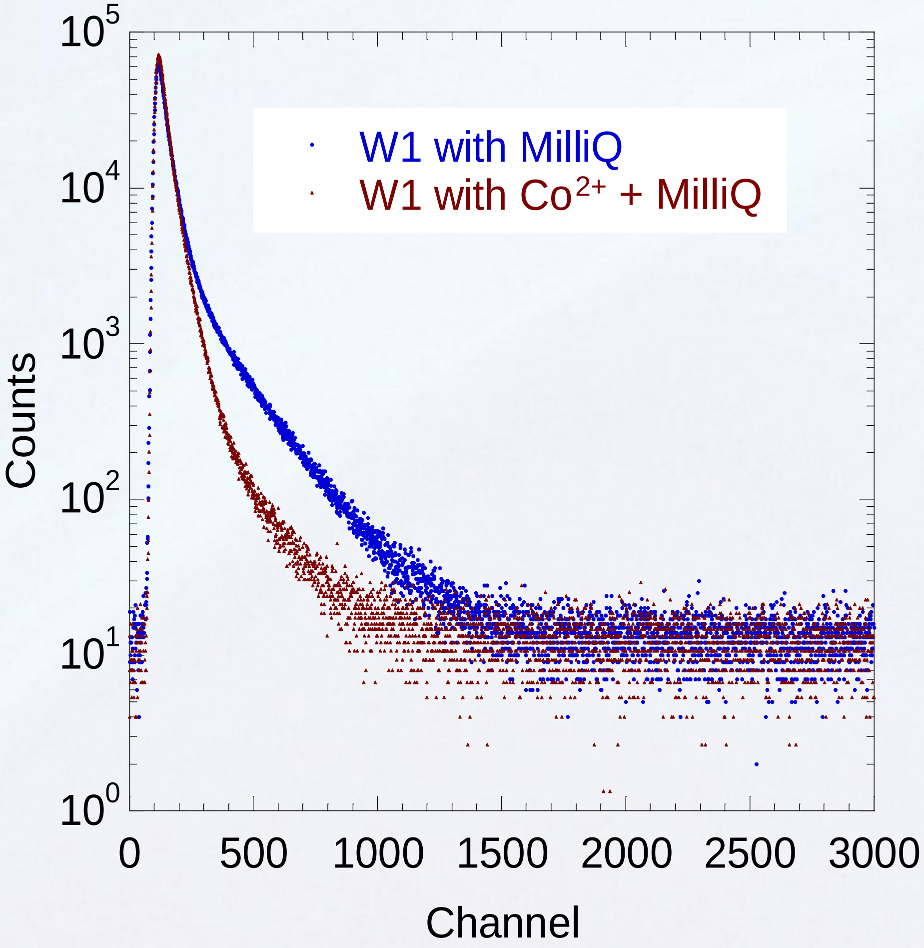
- PALS shows no change in nanoporosity.
- BET shows no change in surface area.

$$\frac{1}{\tau(r)} = \lambda(r) = \frac{1}{4}(\lambda_p + 3\lambda_o)\left[1 - \frac{r-\Delta R}{r} + \frac{1}{2\pi}\sin\left(\frac{2\pi\cdot(r-\Delta R)}{r}\right)\right]$$

Basic protein structure appears to be conserved

Metal binding: Effect of porosity

University of Tsukuba



- ➢ Wool samples saturated with Co^{2+} (~0.4M)
- ➢ Ps is formed, counts represent annihilation of all 3 components
- ➢ Decrease in counts reflects change in number of open pores

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Metal binding: Effect of porosity

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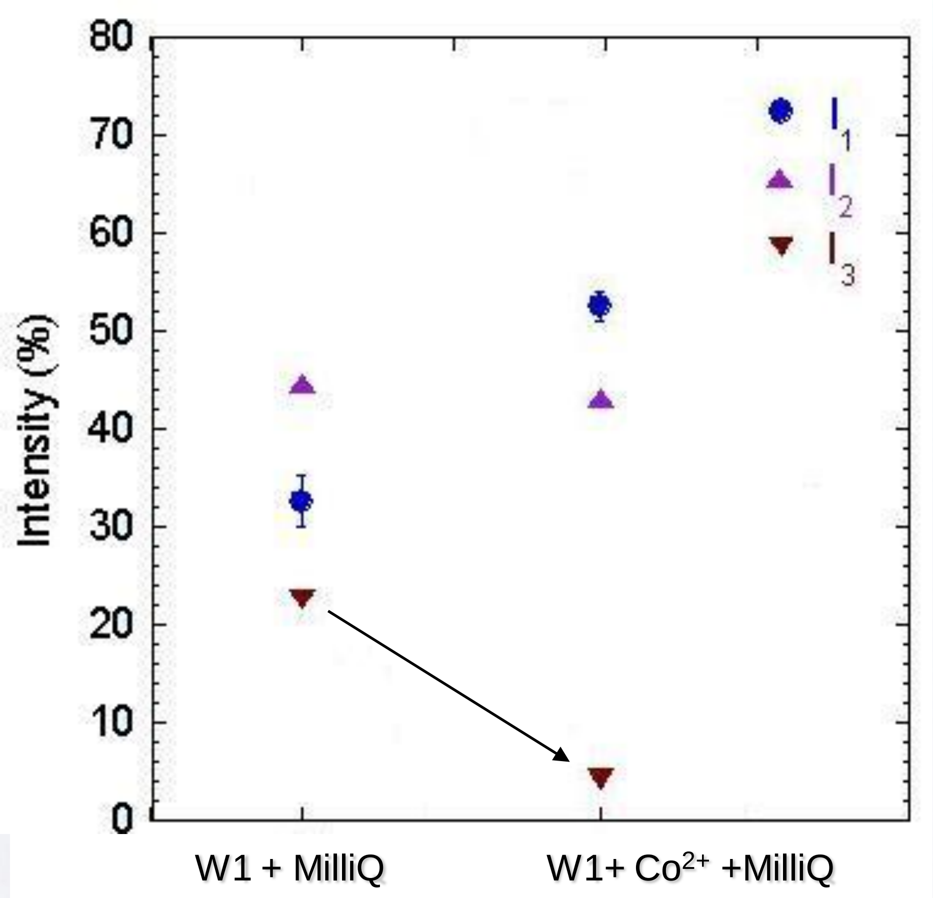
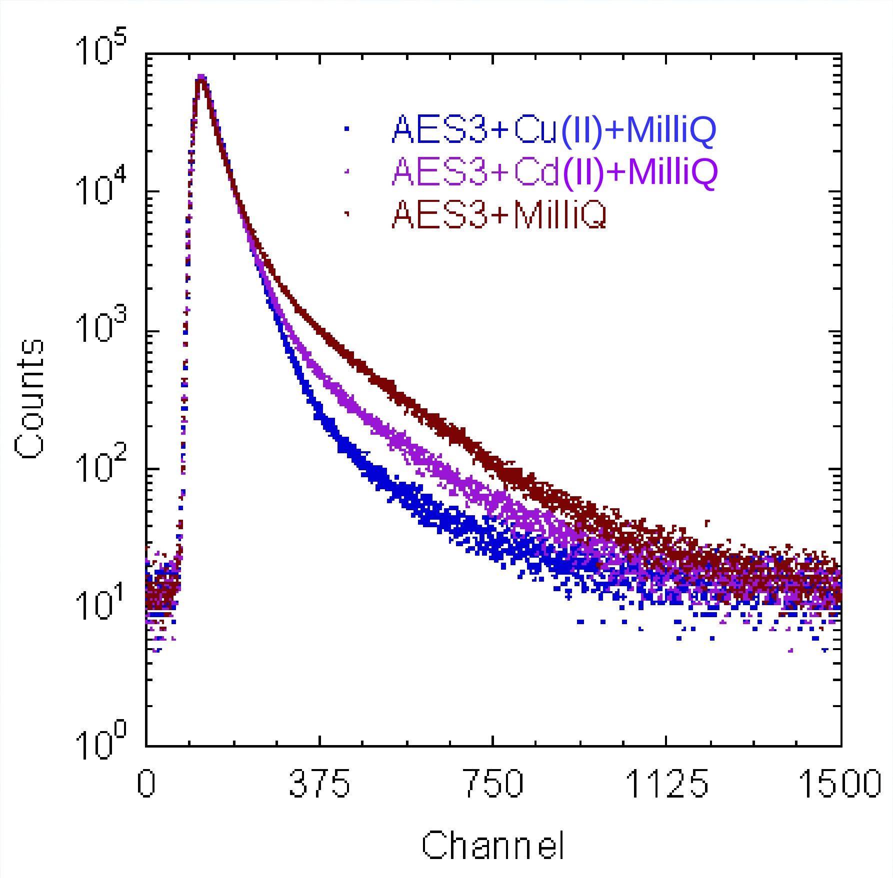
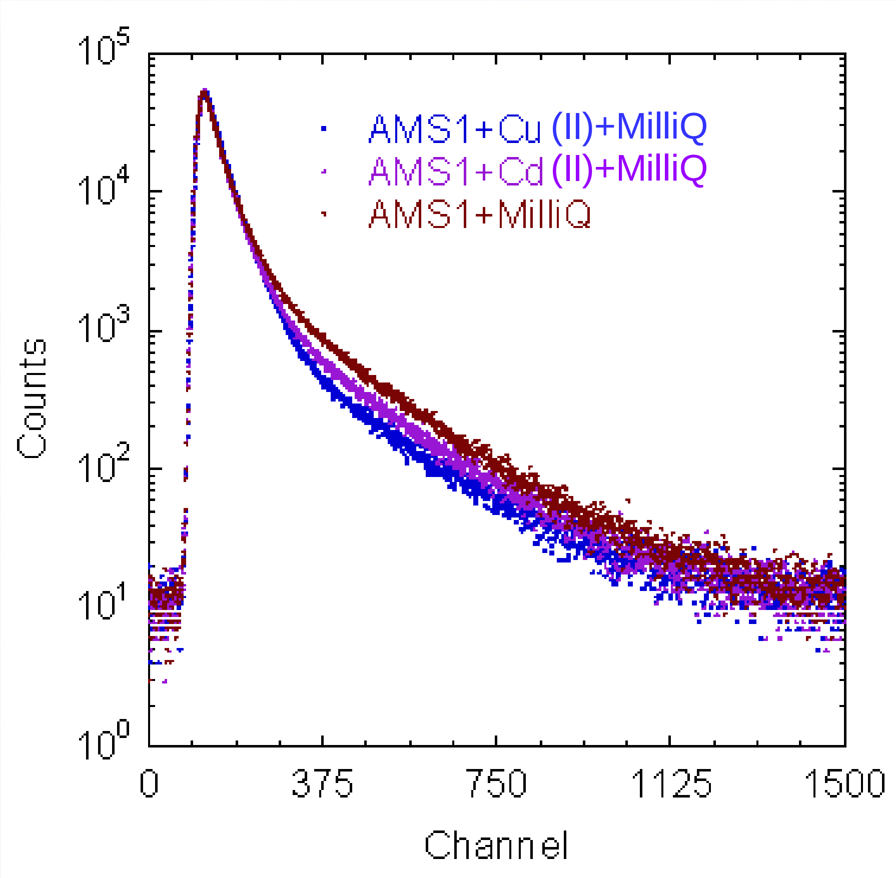


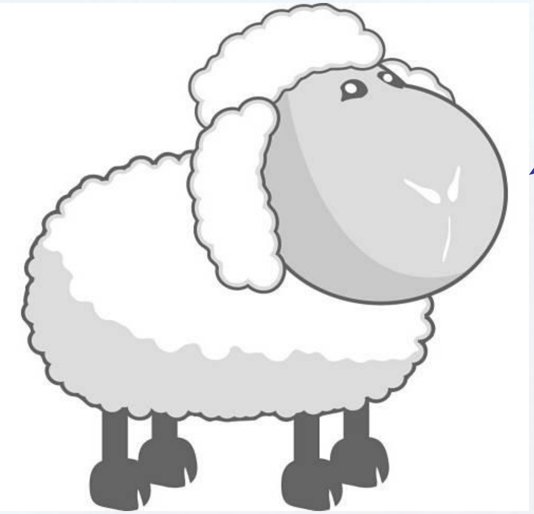
- ➢ Proportion of open nanopores decreases dramatically on saturation with Co^{2+}
- ➢ Some of the Co^{2+} gets trapped into nanopores in protein structure

Metal binding: Effect of porosity





Conclusion



- Metal binding
  - varies significantly with pH.
  - depends slightly on processing and type of metal ion; exception: Co.
  - loading capacity higher (3 to 9x) than commercial resins.
- PALS
  - Basic protein structure and porosity independent of sample processing.
  - Some metal ions trapped into nanopores.
- Use of radiotracers allowed rapid, sensitive and high-throughput analysis.
- Potential application in removal of metal ions from waste streams.

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