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COMPARISON OF STABILIZATION AND LEACHING OF CCA AND ACQ TREATED LUMBER

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Background

As the Canadian wood treating industry converts its treatment of residential lumber from CCA to copper amine based treatments such as amine copper quaternary ammonium compounds (ACQ-C) and copper amine tebuconazole (CA-B) systems, it is important to compare the factors affecting fixation or stabilization of these systems with those of the more familiar CCA. This paper presents preliminary results of effects of variables such as species, solution concentration and fixation temperature on the rate and extent of stabilization or fixation of the copper component of ACQ-C in comparison to CCA-C.

Fixation mechanisms

While there are still questions about the fixation or stabilization reactions between waterborne preservative components and wood, the main effects are thought to be:

CCA fixation:

- Hexavalent chromium (CrVI) drives the process as it oxidizes wood components.
- CrVI is reduced to low toxicity, low solubility CrIII.
- CrIII reacts with and precipitates As.
- The resulting pH increase, reduces solubility and helps to fix copper.

The chromium reduction process is easy to follow qualitatively or quantitatively in the treating plant or research laboratory through the colour reaction between CrVI and chromotropic acid (qualitative spot test) or diphenylcarbazide (quantitative analysis of expressate or leachate from borings).

ACQ stabilization:

- Cationic Quaternary ammonium compound is rapidly fixed to anionic wood at high pH.
- Copper amine is more slowly fixed to wood (mainly lignin) at high pH.
- Some low solubility copper compounds are deposited in the wood void structure

The copper stabilization reaction can be followed by measuring the copper content of expressate or leachate of samples taken at different times after treatment using spectroscopic methods.

Effects of temperature

It is well known that CCA fixation is highly dependent on wood temperature which is affected by both ambient temperature and relative humidity. The fastest reaction rates occur when the wood is exposed to high temperatures and high humidity conditions (e.g., Figure 1).

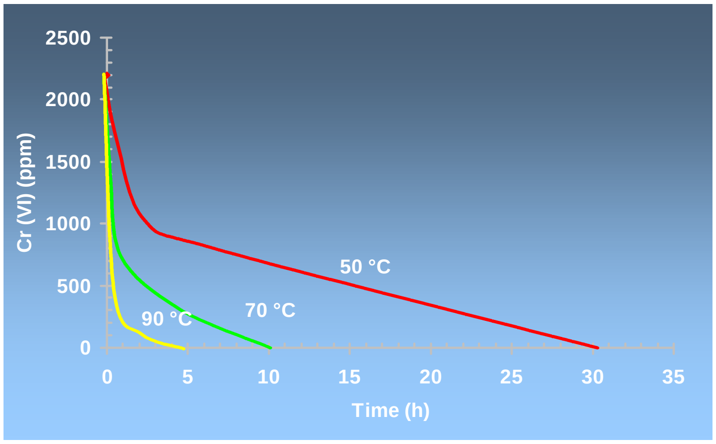

Figure 1: Effect of wood temperature on rate of CrVI reduction in CCA treated red pine sapwood

It has also been observed that copper amine preservative reactions with wood are temperature sensitive with rates of stabilization increasing with increased wood temperature (e.g., Pasek). Figure 2 shows different copper stabilization rates for commercially ACQ-C treated spruce/pine/fir lumber stored at ambient temperature or subjected to different temperature humidity conditions. The plotted values are copper concentration in leachate from borings taken at different times after treatment. It is clear that the rate of copper stabilization is highly dependent on the wet bulb temperature which is the best indicator of actual wood temperature.

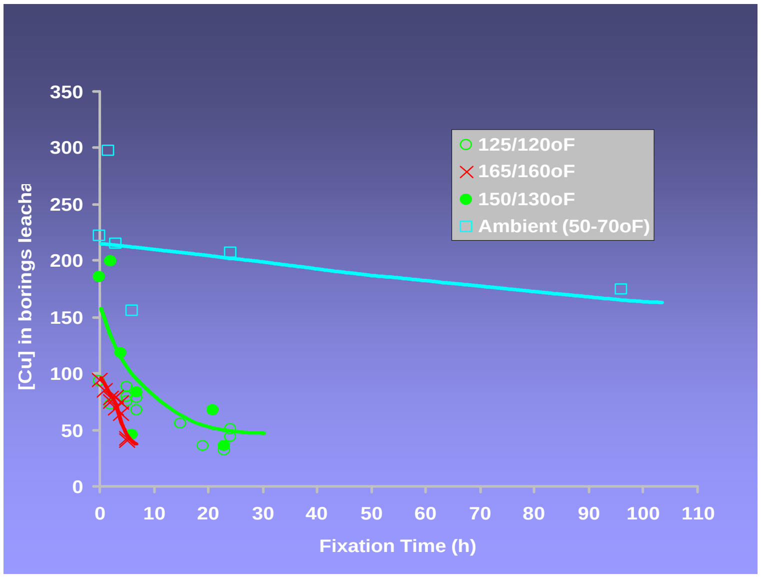

Figure 2: Stabilization of copper in ACQ at different temperatures

Wood species and sapwood/heartwood effects

The rate of chromium reduction after CCA treatment is highly species dependent (Figure 3) and appears to be most related to the presence of wood extractives. It follows from this that heartwood should have faster chromium reduction rates than sapwood as confirmed in Figure 4.

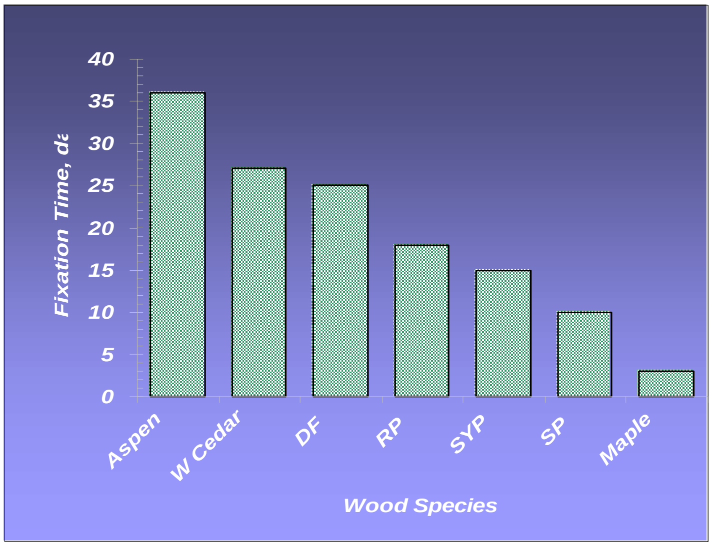

Figure 3: Effect of wood species on time to chromium fixation at 21°C (sapwood)

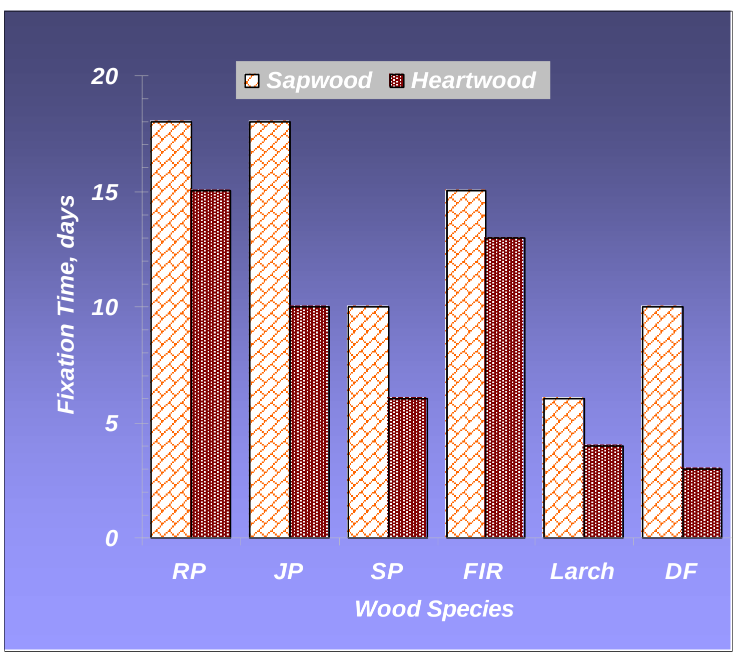

Figure 4: Comparison between sapwood and heartwood rates of chromium fixation in CCA treated wood at 21°C

Effect of solution concentration

It is well known that the time to complete CCA fixation increases with increasing solution concentration.

Less is known about how the above factors affect ACQ stabilization, so we undertook a study on effects of wood type, stabilization temperature and solution concentration on ACQ copper stabilization rate and leaching.

Methodology

A supply of SPF, red pine and aspen lumber and ACQ-C treating solution concentrate was acquired. Small-scale laboratory testing was conducted to quantify the different variables. Small wafers representing sapwood and heartwood of spruce, fir, red pine, jack pine and aspen were cut (5mm X 20 mm X 50mm). For each study, 5 replicate wafers were used. Retentions were estimated from the solution uptake and concentration. Five solution concentrations were used, 0.5 % 1.0 % 1.5 %, 2.0 % (all variables) and 2.5 % ACQ for a limited number of samples.

Samples were allowed to stabilize without drying either at room T (21°C) or at 50^{o}C. At different times after treatment wafers were squeezed in a press to express treating solution and the solution analyzed by XRF for copper content. The change in concentration of the expressed solution relative to the initial copper concentration was used to estimate the time to stabilization and the % of copper reacted when stabilized.

At the end of the stabilization period, wafers (individually) were stirred in 50 ml water for 24 hours then the water changed and repeated for an additional 48 hours and then for 11 more days. Leach water collected at these three different times was analyzed by ICP for copper content and the % of total copper leached determined.

Results and discussion

Stabilization results

The stabilization results at 50^{o}C storage conditions for jack pine sapwood, spruce heartwood, red pine sapwood and aspen sapwood are shown in Figures 5 to 8. All softwood species reached an approximate equilibrium in one to two days at this temperature. Lower retention treatments appeared to stabilize faster than high retention treatments as has been observed by others (e.g., Pasek 2003). The aspen required longer (about 4 days) to stabilize due to its anatomical structure that requires copper to diffuse longer distances from the treated vessel elements. By comparison, most CCA treated wood stabilized in 16 hours or less at this temperature.

The concentration of unreacted copper in the wood cell lumens at equilibrium was higher for higher concentration solutions; when the values were converted to % stabilized. There was some suggestion that higher retention treatments had a lower % of copper stabilized but this trend was not consistent. In general, the copper stabilization was in the range of 70 – 80 % for all wood species. This suggests that the stabilization mechanism is not very dependent on the chemical properties of the wood. However, additional work is needed to see if this holds for species with high extractive contents such as Douglas-fir heartwood, cedar heartwood and soft maple.

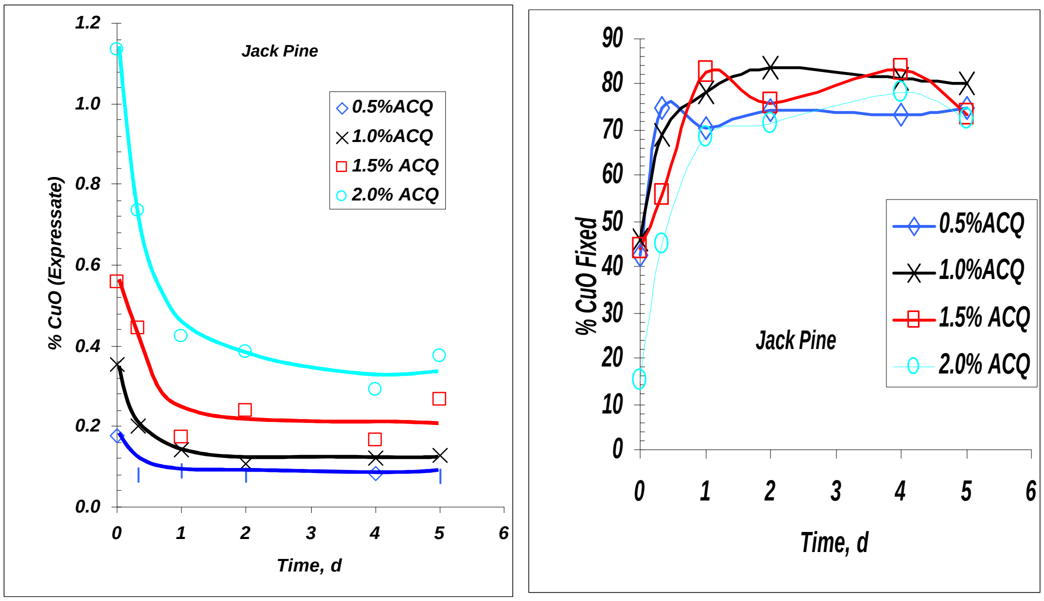

Figure 5: Stabilization of ACQ in jack pine sapwood

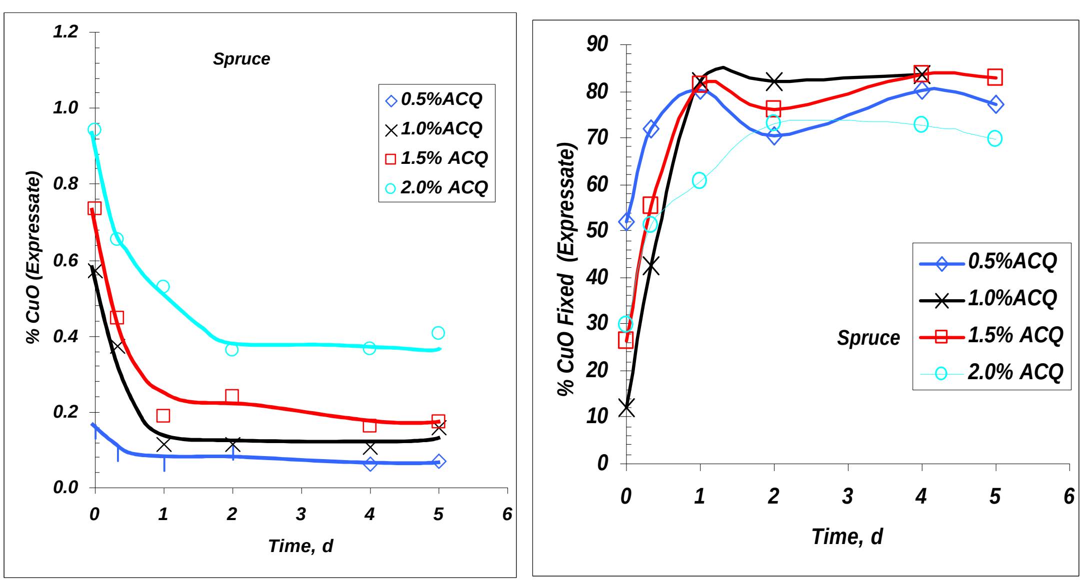

Figure 6: Stabilization of ACQ in spruce heartwood

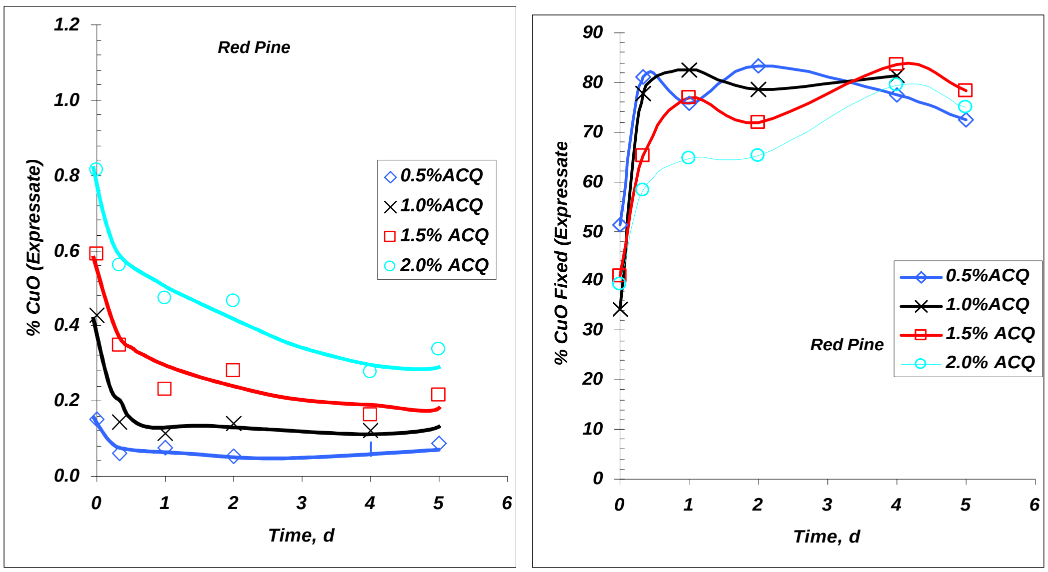

Figure 7: Stabilization of ACQ in red pine sapwood

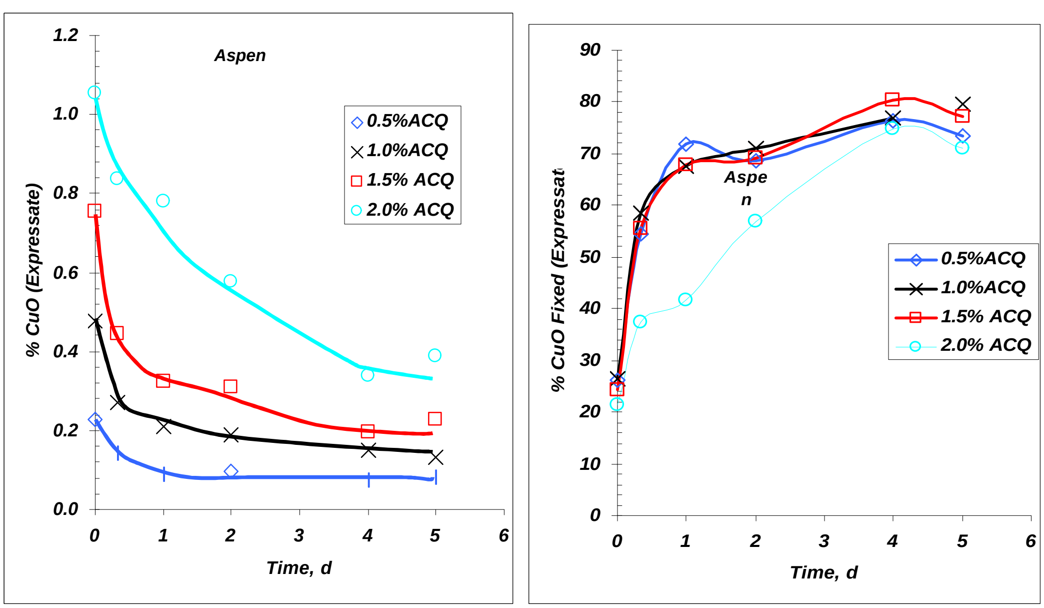

Figure 8: Stabilization of ACQ in aspen sapwood

Samples stabilized at 21°C did not reach the same levels of copper reaction with wood even after about 3 weeks when this study was terminated (e.g., Figure 9 for spruce and red pine). Additional study on red pine samples indicated that approximately 45 days period of stabilization is required for the copper to reach the same levels when there were stabilized at 50^{o}C. It is clear that at lower temperatures, a much longer stabilization periods is required.

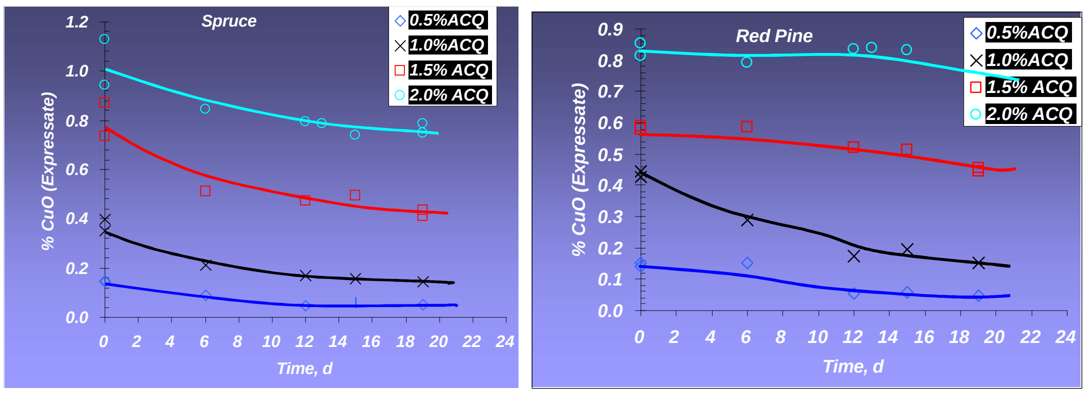

Figure 9: Copper stabilization in spruce heartwood and red pine sapwood at 21°C

It is clear also that in this case, the time to stabilization is higher with higher solution concentrations.

Leaching of copper

The 48 hour copper leaching from the wafers stabilized at 50°C is shown in Figures 10. There was no consistent effect of wood species among the three softwood samples on copper leaching. The concentration in the leachate increased with increased retention in the wood, but the % leached remained constant or even decreased with increased loading.

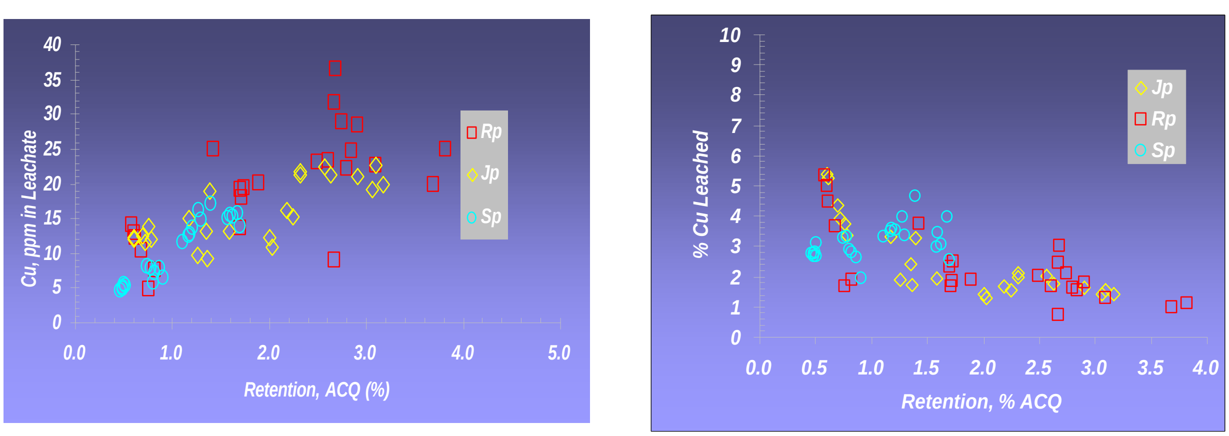

Figure 10: Copper leaching from wafers stabilized at 50°C

For samples stabilized at 21°C for 20 days, (Figure 11), the leaching losses were much higher, especially at higher solution concentrations, confirming that the copper was not stabilized to its full potential even after almost 3 weeks at this temperature.

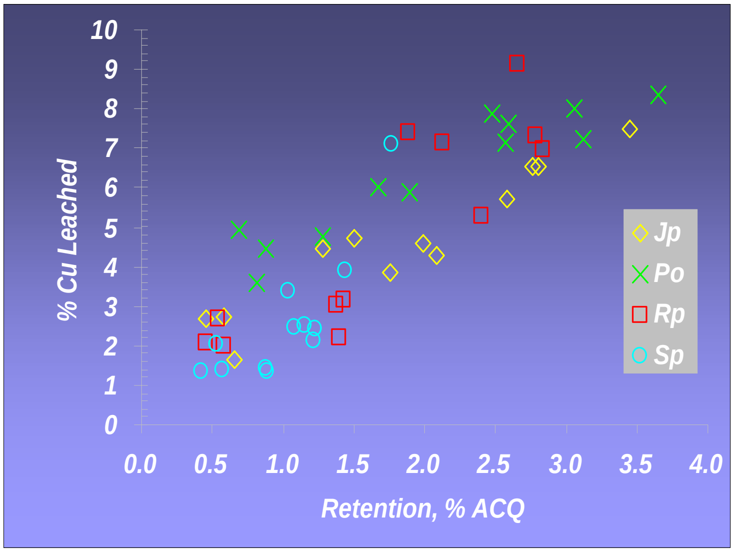

Figure 11: Copper leaching from wafers stabilized at 21°C for 20 days

Summary and Conclusions

Both CCA and ACQ fixation or stabilization are affected by several variables and there are indications that ACQ is more temperature dependent but less species dependent than CCA. It may be necessary to adopt accelerated (high temperature) fixation treatments to ensure that ACQ is adequately stabilized before it is put into service.

Relevant papers

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