>>*Moderator:*   All right, good afternoon, everyone. Thank you for joining today's call. A couple of housekeeping things here. Everyone that is an attendee is joined in listen-only mode, meaning we don't have access to your cameras or microphones. If you have any issues, try connecting through your phone. And if that does not work, go ahead and just shoot us a line in the chat bubble here. And any questions throughout the call, go and ahead and drop it in the chat as well, and I will hand it over to Deb. Thank you.

>>*Deb Agarwal:*   Thank you and thank you all for joining. This is the latest seminar in the NOWEE webinar series. This one's going to be part of the modeling and simulation focus of the portion of the webinar series. We've got a set of these webinars that are focused on that. And I'm really excited to have Aaron Wilson from the Idaho National Laboratory as our next – as our presenter for this seminar. He's a research chemist, whose specialty is chemical separations, and he leads that group at Idaho National Labs. He's got a water treatment background. Particularly he's been working on solids precipitation and zero liquid discharge opportunities as well and solvent-driven separations. So without further ado, I'd like to turn it over to Aaron. And as was already said, feel free to put any questions in the chat, and we'll queue them up and get them answered during the seminar and after. Thank you so much. Take it away, Aaron.

>>*Aaron Wilson:*   Thanks a ton, Deb. Yeah, I'm Aaron Wilson. I'm a research chemist and I've been with Idaho National Lab for about 11 years. Originally, I was trained as an organometallic and organic chemist in electrochemistry. But since I've been at Idaho National Lab, I've predominantly worked in water treatment. And all this work I've done in water treatment has really driven an interest in electrolytes and application. I mean if you're thinking about this right now, you're using your potassium ion channels, which are heavily depending on solute behavior. And just from manufacturing materials to making systems work like batteries to just all sorts of natural systems around us, electrolyte behavior is important, so this is something I'm really excited about.

And, as Deb mentioned, I've been working in the space of water treatment, and I've been more recently focused on solvent-driven aqueous separations. And so these can be divided into two major categories. The first is solvent-driven fractional precipitation. And in this process on the top here, you have an organic that dissolves into some sort of concentrate and drives a salt normally to precipitate out as a solid. Oh, great.

Okay and so that precipitates out as solid which – and then you have an aqueous phase here rich in organic, which then had to go through a regeneration cycle where you get the organic back and you end up with a depleted or softened solution coming out.

Another form of solvent-driven aqueous treatment is water-selective extraction. A lot of people are familiar with solvent extraction where you use ligons to pull ions from an aqueous phase into an organic phase. This is similar but different. You have an organic phase that comes in, and you have water selectively going to the organic phase, which concentrates the aqueous phase to some point where it's separated or you actually generate solids, which are separated in a ZLD process. The organic phase is then water-rich and it goes, again, to an organic aqueous separation process, and you get purified

water out of this process. And this can be applied to zero liquid discharge and material drying.

So let's see here. Okay and so, like I said, the area that we're interested in is the area that is challenging for most water treatments, which is the solid-liquid equilibrium boundary. And that includes sparingly soluble salts with softening and highly soluble salts with ZLD. And more recently, we've found that a lot of this experience we're gaining in kind of the water treatment space also has applications in hydrometallurgical space.

We recently joined the Critical Materials Institute. I was able to bring on a post doc, Caleb Stetson, a couple actually, Hyeon Lee. And this is work done by Caleb in which we've taken collaborators at Ames Laboratory—the DOE Ames, not the NASA Ames— supplied us with cobalt samarium magnet leachate. And it's this rich red color, and we add an organic solute to it, dimethyl ether, which I'll talk about more. And when we do that, we precipitate out salts in crystalline form. And by varying conditions we can actually favorably precipitate cobalt sulfate or samarium sulfate, and we end up with a really depleted solution, and this was super exciting.

And so the organic solute we're using is, like I said, dimethyl ether. And dimethyl ether's a unique solvent. It is a condensable gas, but it's highly polar. So a large fraction of DME goes into water and a large fraction of water goes into DME. And then since it's condensable gas, it can be easily removed. And so this is – and it's cost-effective. It tracks with gasoline in terms of price. It's vapor compression. Its cycle is very well-known. In fact, it was the first commercially-used condensable gas used as a refrigerant. It doesn't form explosive peroxides like other ethers, and it's used in consumer products: over-the-counter wart remover as well as for processing of food both in Europe and the United States. So this is what this process looks like in terms of what we're doing. We can start here with the DME gas, which we compress. We don't have to liquify it. We just need to compress it so that it goes into the aqueous space. And when the DME goes into the aqueous space, salt is precipitated out. And then we have a DME-rich aqueous phase, which we take to a separation system, which is driven by reduced pressure and increased temperature to regenerate the DME. And we've achieved hydrometallurgical separation in the process.

And we've basically been marching through a lot of different systems in demonstrating this works. It can knock out concentrated sodium chloride, gypsum, calcium sulfate, silicate, neodymium cobalt sulfate, nickel, samarium and sulfate. And these are the just the ones I have slides for. This was our initial report to the critical materials hub in terms of performance. And so we started with this leachate that was mostly cobalt and a lesser amount of samarium and even less iron. And we got high purity samarium out of the system, which was super exciting. And then when we went back and we started varying conditions, we found that we could drive out samarium selectively or cobalt selectively, and we could do this in a sequential process, which was really exciting.

We have related work for DARPA in terms of solids decontamination. They're interested in taking waste to usable materials like a lot of people are interested in doing, specifically

plastics. And so to kind of meet the goals of DARPA, we looked to the solvent extraction industry, which is booming right now. Due to legal changes in Colorado, there's a number of companies that will sell you condensable gas extraction systems for marijuana products pull materials out of marijuana. And this system here is designed to operate with propane and n-butane and isobutane. And we're modifying it to work with DME, and we can further modify it so that instead of treating solids, we can treat solutions with it, and so this is kind of exciting.

So when we first started looking at this fractional precipitation process, DME driving salts out of solution, we wanted a salt that would reach high concentrations and we could observe its behavior, and so we went with sodium chloride: common salt. It was a good, simple choice. And what we found – and we went to the literature and there's only four examples of ternary systems with water sodium chloride in a miscible organic solvent, which seemed like a real lack of data on our part. So we studied – I think we did 12 examples ourselves. One was a repeat. We ended up with 14 total ternary systems in terms of how we – observing the solid-liquid equilibrium between – as organic is added into a salt solution. This is a solid-liquid equilibrium line, and then these are the liquid salt-induced liquid-liquid equilibrium lines that kind of curve here.

And what we found was starting from a saturated sodium chloride solution, binary solution with just water and salt and we added organics to it, if we counted the salt as hydrated, we got a one-to-one displacement of that salt for every organic we added, which was really exciting because salt at high concentrations, the air saturation is supposed to be highly non-ideal. Organics at highly dilute conditions are highly non-ideal. And we're seeing molar behavior here, one-to-one molar behavior here, and it's certainly not driven by dielectrics. And I won't go through that in detail, but it just doesn't match up. And so this displacement is pretty much regardless of which organic solvent you throw at it. So what is going on here?

So go to the literature. I'm really interested in finding like the raw data on electrolyte behavior. So I go to this – one of the things I do is go to this paper that pulls data from Robinson Stokes and I'm like I'd love to the see the 1-1 salt, the 2-1 salt, the 1-2 salt and the 2-2 salt all plotted together. And, actually, I'd rather see the activity of these solutions rather than the theoretically modified versions on activity coefficient and _____ coefficient, so I'd prefer just straight solution activity. Get close to the raw data. Except I realized quickly that there's no barrier-free electronic repository of this stuff and then COVID hit.

And so what we decided to do was to actually create a database that is barrier-free. And we compiled more than 500 binary datasets of vapor-liquid equilibrium data from over 100 references, and we put this into a database that anybody can access. This link is live. We actually are still getting the last few bits of data transferred over. There's – we had a cyberattack at INL and our DMZ, which is something to do with your web interface apparently, slowed us down for a little bit. But we're getting back on track, and this is all out there. You can pull the data into graphs if you'd like. It's really easy to search, really natural search function. You can get tabular form. You can download it as a CSV file. Or

if you are modeling in Python or R or whatever or any other software, you can call our data directly and you can actually scrape our entire database. And I encourage you to scrape our entire database so that it's backed up elsewhere, so completely open barrier-free to help people develop stuff.

So I wanted to get at this data because I wanted to look at mass action phenomenon in electrolytes, namely two main things I wanted to look at. And that is ion paring, which is well demonstrated in terms of electric chemistry as well as spectroscopy and other techniques. And then solute solvation, which we know is important to a lot of solute properties including diffusion and rejection for membranes and a range of other things where hydrodynamic radius is a real driver. And why these aren't considered an electrolyte theory is … anyways, the types of solvation we are considering are not just coronation. So you have the classic Lewis-acid donation of water or some other solvent to a cation, and this is coordination chemistry. This is inorganic chemistry. You also have hydrogen bonding between water and anions. But we would also include clathrate formation, caging formation. Basically, the surface of water around a material that is highly unlike water. And the only – the key boundary, the key determining factor here is that solute energy changed significantly from the bulk solute and is the lifetime of that system in terms of colligative properties sufficient for that to matter.

And so we thought that these mass action phenomena could explain two of the deviations we see in solute behavior. And so, like I said, I wanted to go straight to solvent activity. So AA is solvent activity. One minus AA is a solvent activity residual, and that should be linear to the solute concentration for an ideal Raoult system. If you get a negative deviation, you have less solute than you'd expect, and that can be explained through ion pairing. If you have a positive deviation from this behavior, that implies you have more solute. And that can be explained through hydration when waters are taken from the bulk and partitioned into the solute, and so those were our two theories. Ion pairing is super easy to model for 1-1 and 2-2 salts, extremely easy. Asymmetric salts are a little bit harder but not hard. And this is very similar to what people do to model polyacids and whatnot. It's extremely reasonable to do. We make undergraduates do this sort of thing all the time.

So if we go back to uranyl sulfate, uranyl sulfate is very well-known not to be fully ionized, so let's fully ion pair it. And as soon as we fully ion pair it, we've lost all the negative deviation, and so it's starting to look better. And then we can factor in hydration, at which point you get a really good match with Raoult's behavior. Now, this full ion pairing isn't quite right. The literature values for the actual ion pairing value, which is shown here, it's concentration dependent. It's the second order equilibrium. And once you do that, you have to adjust the degree of hydration to get this linear behavior by two-tenths of a value. But this is starting to look really interesting.

And then the question is how would you model hydration solvation? It's well known that as concentrations increase, solutes have decreasing amounts of solvation. You can find this in the literature in a variety of different places. It can be found including neutron and diffraction behavior and whatnot. Ion pairing complicates this because when you form

ion pairs, you release solvent as the ion pair is usually less solvated than two free ions. There's also changing threshold in terms of what's considered bulk solution and solvate solvents. The energy of the water changes a lot between a water with an activity of one and water with an activity of .1 like you'd find in saturated lithium chloride. So this is a complex process. This is confusing. In our first paper we said, well, we know –

>>Deb Agarwal: Aaron?

>>Aaron Wilson: Yes?

>>Deb Agarwal: Sorry to interrupt. Do you want questions during your talk or would you prefer to queue them up for the end?

>>Aaron Wilson: Maybe the end. Let's do the end. I can flip back and forth for my slides pretty well.

>>Deb Agarwal: Okay, I'll queue them up.

>>Aaron Wilson: If we were in a room, I'd definitely take them as we went. But on here I don't know if I'm fully comfortable with that. Anyways so in our initial pass at this, we said okay, what if the hydration linearly declines with the solute concentration, which actually gave us a mathematical fit of the data. However, we want a mechanistic fit as well as a mathematical fit. And so that pushed us to look at the actual equilibriums involved in hydration. I've got two of them down here, two different frameworks. One is solute reference framework so the concentration of the solute. This is defined by concentration of solute, has some degree of hydration and a water can dissociate just like a proton would dissociate from a polyacid.

And then you could also do this in terms of the solvent concentration, waters concentration in its different states. And this might be more appropriate for kind of the caging behavior. And these two equilibriums are highly related. They differ by N minus 1 over N. And these aren't actually the equilibrium we care about, and so we'll be caring about N minus value over N as they approach N, so these actually become the same value.

So, getting to that what I was just talking about, we can start with some theoretical level of hydration of N, and then we can start dissociating sequentially to the point where we're going to N minus M. If you combined all of these equilibriums, all the intermediates cancel out leaving you with the hydration of N and N minus M to the concentration of water taken to a power of M. We can combine these equilibrium constants into a composite, these flip sides as you move them onto the other side of the equation. And then you can move the equilibrium constant on the other side.

But if we're talking about a system where the solute is at equilibrium, the degree of solvation of the solute's going to be equivalent. So N minus M is actually approaching N. And when that – when you consider that state, which is the pertinent state, this ratio here

approaches N to H2 in terms of it's the degree of hydration on the solute. And so you take this and it becomes the degree of hydration times K equals the water concentration to M. You move K from the dissociation constant over to the other side. It becomes the association constant. And for the time being, we're treating M as two based off of the degree is dissociation we observe. And what this means is that full – pure water K equals the highest degree of hydration.

What's this look like applied to some sodium? We have sodium hydroxide here. If we start adding in hydration to this according to this equilibrium value so what we have here is we've got the sodium hydroxide ionized concentration up here. We've got the water concentration down here in mull fraction. We've got the sodium hydroxide concentration there. And then we start subtracting out equilibrium, the K value times the solute concentration adjusted for the water concentration.

If you apply this, what you do is you start approaching a more ideal type behavior. We actually overshoot it. And then we're going to start adding in ion pairing because these systems are known. All these are known to ion pair, and so you add a reasonable amount of ion pairing that matches up with the literature values that are actually all over the place for sodium hydroxide. But you end up with something that is pretty close to the ideal. And over everything from dilute to saturation, these are just two mass action equilibria. And it's these two constants, these are two values to get this to all line up.

Next thing we did was we looked at some – Hyeon Lee did some calculations on this. And what we found is we were aiming to see if the molecular dynamic model matched either the decline – what I was expecting to see was that the solvation environments around the solute would actually lose solvation. Like they would – there'd be a decline in the degree of solvation or, using our broad definition here, around the lithium and the chloride in the system. That's not, in fact, what we observed. What we observed in the molecular dynamics calculations is the solvation environment's changed a little but not dramatically. What really changed was the degree of sharing of solvent between solute. And so this purple open circle line is the degree of sharing of solute between lithium and a chloride. And it goes up and then it hits a limit and plateaus, and then this green open circle is the solvent shared between chlorides, two chlorides. And then gray is between three chlorides, and black is between four chlorides. And these go to very high concentrations and so this is basically joint solvation.

And this is really interesting because this really becomes relevant when you start thinking about what it would be like to model multi components with this model. Knowing that it is dissociation or ion or solute sharing matters in terms of how you model mixed electrolyte systems. But, luckily, the model I just showed you is valid for both when you're talking about the binary system in the VLE data. Both systems can be modeled in the exact same way, regardless of which is the mechanism given that both mechanisms are possible. But it seems quantitatively this is the dominant – joint solvation is the dominant mechanism.

So this lets us model sodium hydroxide. Here solvent activity is found to be equivalent to the bulk solvent concentration, and hydrosolute concentration is not equivalent to this speciation of solutions and of the solute and solution, which I mean is something that just stands to reason based off of all the experimental data that's out there.

Charge is not a factor for this model at this stage the model. We can model non-electrolytes in the exact same way we model the electrolytes, but we don't need to worry about ion pairing for the most part. And this is great because it lets us cite Einstein's doctoral thesis where he said that sucrose had to be modeled with – in a hydrodynamic sense. And here we're quantifying that hydrodynamic sense in terms of electrolyte theory beyond diffusion and viscosity.

Lithium actually models with a single parameter, which is not actually right. That's too good to be true. Lithium does not fully dissociate. It actually has ion pairing itself. It ion pairs as well and so, if we add that ion pairing in, we can then go on to model the data, and it still models. But in this situation, we have to free up that exponent that is modifying the solvent. And it kind of highlights that we're not 100 percent sure on the nature of the solvent exponent in this equilibria. Is it 2? Is it around 2? How do we model it?

But if we have all three variables—the exponent, the hydration equilibrium and the ion pairing equilibrium—if those are all free, it's too many degrees of freedom, and we don't get convergence. But if we limit it to two of those values, we get extremely good convergence in terms of looking at the variable space for these systems. Like you can – they are – one is increasing, effectively increasing solute concentration. One's decreasing solute concentration. So there's a counter behavior but the functions are different. And so you end up with a very tight fit over what is – in terms of convergence. So this is exciting to see. Sodium chloride when we're looking at the – our initial model was a challenging solute to model. And so we were happy to see that this converged nicely under this model.

And so that's what we have here, so we've just taken an ion pairing. We're applying ion pairing, which reduces the amount of solute – of modeled solute. And then we're adding hydration, which increases the concentration and so this is just the ion pairing element in yellow, and in green we have just the hydration element. You add those together, and you end up with blue, which matches up very closely to Raoult mixing. And so because this is a mechanistic model, it should integrate better with multiscale models that need to go from not an engineering basis, not just a good fit, but an actual mechanistic basis so that other phenomena can be brought in and considered, whether it's surfaces or whatever it happens to be. And so we have – currently we have a mass action analytical model that matches well with data from a numeric molecular dynamic model and all sorts of – and we're basically saying if there's any experimental data out there, it should be considered in this model.

So back to our sodium-chloride system. We're seeing this one-to-one displacement. If we apply this model that I just talked about to both solutes at the same time, what we end up

seeing is not a one-to-one displacement but a constant concentration of sodium chloride. So basically it's not displacing the sodium. Sodium chloride is being displaced to maintain concentration. And so this sort of graph is something that makes sense to me because I've looked at it quite a bit and considered it a lot. But it's actually really useful to look at this in terms of what it physically looks like. So if we take this as a two-dimensional projection of sodium chloride at saturation with ballpark correct numbers of water molecules to ions and within an integer value there at the correct values. And so we have solvated solutes. We have ion pairs. We've got shared solvent. These aren't all accurate. And then we've got bulk solvent with the blue halo.

If we add some dimethyl ether to this, two dimethyl ether, which is actually a lot of dimethyl ether, what happens is the dimethyl ether sucks some of the bulk water up, which decreases the concentration of the bulk water, which means that solute has to precipitate out. That salt as it precipitates out releases water which is also used to solvate the DME. So a fraction of the DME solvation is from the bulk of fractions from the solute that precipitates out. And this actually results in a – so this is anhydrous data. This was our initial model, and the is the equilibrium hydration and ion pairing model that we end up with the speciation model and we end up with this really nice flat line with SLE boundary up here. And then we end up with this kind of wonky curve for the salt-induced liquid-liquid equilibrium, which is kind of where we're going now. And I'm going to fly through some stuff, but it's more speculative.

But solvent is often split into immiscible, partially miscible or fully miscible. I think fully miscible binary solvent, water solvent systems is actually more things that just one thing. It needs to be differentiated more. You can have things that are fully miscible on a molecular scale, but you can also have super molecular structuring in fully miscible things in which you have basically an organic phase and an aqueous phase that are miscible on the sub-wavelength scale, so you wouldn't see it with light scattering, but it's still there. And experimentally this is being demonstrated with diffusion studies and quenching studies and a variety of experimental studies, but I think this is something that's emerging.

And if you add in this super molecular saturation into this behavior, you can take that curving line and actually the MOS solubility ends up starting to look pretty linear. And that's basically a constant organic solute concentration once fully modeled in the aqueous phase. And this lets us kind of jump into looking at how these fractional precipitation processes can be modeled. So we understand where what the solute defines is basically the SLE boundary out to this invariant point between solvent and the solute.

Now with this solvent boundary here, we can just take other solutes like calcium sulfate and project them out and get some idea and start being able to predict their solubilities. We aren't there yet, but we're aiming to get there. And for the time being, we've got some kind of simple rules. Solutes close to saturation will precipitate in a fractional precipitation process that's solvent-driven fractional precipitation solvent. Solutes with low saturation will preferentially precipitate. And solutes with high degrees of hydration will also preferentially precipitate, and that's informative.

In terms of the water-selective extraction, that's more understanding how this aqueous or this organic phase here varies in water composition with the aqueous phase and so in terms of the salt concentration of the aqueous phase. And so we can take that last bit we were talking about previously and look at how adding salt to the aqueous phase affects the organic activity in the system. And so what you see here is as salt is added in, the activity of the DME goes down or the organic goes down and but then it ends up hitting a plateau. And that's kind of – that is what is observed with other experimental systems like this. And so, again, we're still working through this.

And so at the end of it, I'm just coming back to the model. So this meeting is about looking at modeling and simulation, and my interest is in modeling electrolyte theory and solution theory concentration behavior. And so what we have here is this really nice fit that is not the only mass action model out there. There's a few other mass action models out here, but this is the only one that is using ion pairing as a second order reaction. This is kind of interesting. The Van 't Hoff index, which we're all familiar with from like the origins of electrolyte theory, is not secondary. It's first order. And the reason it's first order or it works as a first order is I think the Van 't Hoff index is a composite of ion pairing and hydration behavior. That is what was observed and it works out to be roughly first order. But if you take this to the higher concentrations and want this to behave properly, you need to break those two apart.

And, yeah, so second order ion pairing, a degree of hydration based on a solvent concentration and this matches with all sorts of experimental data, whether it's neutron diffraction studies, molecular dynamics. And I think it's set up well to be advanced further so that it can address a lot of physical boundaries and physical behaviors.

I've had – I've worked with a really great team in this space. The work I've shown is basically coming from two places. It's an LDRD that has allowed us to kind of jump into this DME-driven separations, and this has been a collaboration between MIT and INL. John Lienhard and his graduate student Zi Hao. And Akshay is a post doc in the group. He's been collaborating with Caleb Stetson, Hyeon Seok Lee. And Chris Orme is a researcher on our team. And we looked at a lot of the sodium chloride MOS stuff together. And so I'm looking at these models. John and his team are looking at kind of more conventional models. And it's a really good collaboration there.

And then the hydrometallurgical separations are a product of a CMI project, which started last summer and really got going when Caleb Stetson and Hyeon got here in the fall. And so once Caleb was here, he jumped onto this project as his primary space of work. We started a collaboration with Denis and Ikenna at Ames Laboratory. They were able to get us some leachates, and so we've been looking at leachates, at stripping solutions, and we've gotten these really great separations. And so that's, yeah, that's what I had to share today and I'd love to take questions.

>>Deb Agarwal: Yeah. Thanks, Aaron. That was awesome. So we've got one question so far. So salt in total dissolved solvent state like 140,000 PPM can be extracted

and then economically removed from the water stream like can produce water for oil and gas processes?

>>*Aaron Wilson:*   Okay so salt, okay, so sodium chloride. So sodium chloride so highly soluble salts are challenging to do the fractional precipitation on them. In the case of sodium chloride, you're more looking at saturation limit, which I'm pretty sure is 260 TDS, 260 KTDS. And what happens there is we can knock out, I believe, 35,000 TDS, which is like seawater, but it's just the very top end of saturated sodium chloride. There is actually – there's patents on this so Chevron—I'm not sure when it was but it was decades ago—went after producing chloride through this mechanism in a cost-effective manner. Now, the most important – one of the most important things with doing this solvent-driven separations is you've got to recover the solvent. Our targets for solvent-recovery are always five nines so 99.999 percent. And if you start losing more solvent, it really cuts into the economics of the process. So complex, complex answer. The solvent processes are definitely used to separate out some salts or they at least have been explored in the past. I'm not exactly sure if and how they're applied in the industry at this point.

So but if we – let's see if we can't get back to the beginning. We look at these systems. We can – DME can be used in this water-selective extraction process, so we can send dry DME into this and we can pull water out of these high-saturation brines and just concentrate them up, and you can go ZLD. And then if there are, say, scalants or other metals in this, those things will get knocked out according to the thermodynamic rules we're trying to understand. So calcium sulfate, silicate scalants will just be like in this system they'll be knocked out according to this top system right here at the beginning. So DME goes in. It knocks those scalants out here, and then you can start doing water-selective extraction so yeah.

>>*Deb Agarwal:*   Thanks. So on a practical level, what is residual contamination of the solvent? I think you mentioned that since you're trying to go after five nines. But also what is the energy cost in the separation?

>>*Aaron Wilson:*   Yeah so that's a great question. So we're doing TEAs on that, and there's a lot of different mechanisms to regenerate and do like the DME water separation. And we're exploring a variety of different ways to do that, and so in this top – in the bottom system there are basically nine organic molecules for every water molecule. And in the top one there are – this is – or by mass. This is … let me see if I can't get it right. This is 10 percent water by mass in the bottom, and it's 30 – it's a third organic by mass on the top. So the energies of these two vary by about 20 ballpark in a sense. But it's the actual end removal that is the real driver, so we've got TEAs that we're developing. We're looking at like 20 to 40 kilowatt hours per ton water treated. And it will be lower for the top process, higher for the bottom process with DME so …

>>*Deb Agarwal:*   Thanks. So what about if you had a more complex water matrix like seawater instead of sodium chloride?

>>Aaron Wilson: Yeah so it's more complex. That's a great – like great question. So one of the things that I have sitting in one of my top level folders is basically ternary systems of various chlorides. Like there's some great papers out there with ternary chloride systems and seeing if we can't model those well. And some systems will be affected more so by the complexities but others, it's not going to be a big difference. Like it's not going to be a massive difference. And so in kind of the hydrometallurgical side, the rare – the critical materials, the transition metals and the lanthanides, we're seeing ballpark similar separations for components as we would in the pure state. Now that's not completely true, and there's actually a lot more complexity in those systems than I'm able to talk about right now. We're actually filing some IP supposed to be this week. They're a little late on that so anyway … anyways, once that happens, I'll be able to talk about that side of it some more, but it's super interesting, though.

>>Deb Agarwal: Okay, so 2-2 salts ion pair at much higher levels. Can a conversion to 2-2 from 2-1 improve the amount of salts extracted?

>>Aaron Wilson: So that kind of – that's a great question. So I imagine 2-2 and 1-1 salts both when you look at precipitation, it's really the ion pairs that are driving precipitation. But when you do the equilibrium constant it's really like the KSP. It doesn't matter. That's just an intermediate state so it kind of comes out in the wash. I guess it just ends up being the total solubility of the materials. Now, one thing that is related to that is we are modeling the hydration as assigned to every solute in the system assuming full dissociation so it's an assumption. We can't discriminate between the solvation of the ion pair, the solvation of the ion, the solvation of the cation.

Now, one thing I didn't put up here which I'm wishing I did is a comparison, a periodic comparison of trends. And we actually see an increasing degree of hydration as we go from fluorine to iodide so as you go to fluorine, chlorine, bromide and iodide, your halite is getting bigger, and we see a larger degree of hydration as you go up. And that can be explained through greater dissociation but that's not it. It doesn't match the data. So it looks like the degree of hydration's increasing with the anion, which is just a volume type effect of what it takes to take care of the surface of that material so yeah, anyways, I can go off on tangents.

>>Deb Agarwal: Thanks so have you looked at temperature swing solvent extraction?

>>Aaron Wilson: Temperature swing solvent extraction. Oh so that's not – so ours is in a sense a temperature swing, but we vaporize our solvent in the process. But what you're talking about there is solvents so we're looking at the bottom system where the solvents have different solubilities of water at different temperatures. And you could even go to the point where you have lower critical solution temperature type behaviors. There are some great – I know Yip at Columbia is doing some work in that space, and there's been – there's a couple other teams out there working that space, and they're doing some great work. And if you want to email me, I'll point you to them, but it's definitely interesting.

For me what I see as the challenge there is when you go to those heavy – the systems that do this are heavier molecules. And if you're going for that five nines recovery and these are equilibrium processes, you're going to end up with those materials in the purified water. And you're even going to end up with those materials in the solids, and you got to recover that. Otherwise, it becomes more scientifically interesting than it is industrially interesting so yeah.

>>Deb Agarwal: Thanks so you've got some kudos on the IDTS as a terrific and long-needed resource.

>>Aaron Wilson: I appreciate that.

>>Deb Agarwal: Yeah, I see that it currently only contains data for binary systems. Are there plans to add ternary system data?

>>Aaron Wilson: So, yeah, it's just another resources and I would be like so like getting into this space was an experience in trying to learn how to plot ternary systems. And I got to say Akshay, former student of Manny Alamalicks, currently a post doc with John Lienhard, his Python skills were what took us from these terrible Excel mods into fairly decent web presentations. So I would really love it if we could get a web-based ternary applet and I don't know. It just takes resources. It's actually the database construction is so routine and streamlined. So with that we have – the paper associated with that database has been submitted. So that's submitted and that should be appearing and that'll be like our proxy for citing this stuff. And so, yeah, I want to get ternary data in there. It's just a matter of getting a little bit of resources to pay the web developers and the database designer and then sullies to go out and collect or like interns to go out and collect the data and get the data entered into the system so yeah, no, it's – I would love to make that happen. And even if I don't do it but I drive like NIST to do it by embarrassing them, I'm thrilled to do that too so yeah.

>>Deb Agarwal: Thanks so much. So in solvent-driven water-selective extraction, can you substitute MVC by thermal energy?

>>Aaron Wilson: Solvent so … okay, okay so at what point? Were we talking about the solvent recovery step here? I'm going to look for this, see if I can't find it. I'm not seeing it in my –

>>Deb Agarwal: Yeah, it's not in yours because they sent it directly to the host, but I could read it again.

>>Aaron Wilson: Could you say it one more time?

>>Deb Agarwal: I can read it again.

>>Aaron Wilson: Yes, please.

>>*Deb Agarwal:*   In solvent-driven water-selective extraction …

>>*Aaron Wilson:*   Yes.

>>*Deb Agarwal:*   … can you substitute MVC by thermal energy?

>>*Aaron Wilson:*   Yeah so I'm going to interpret that—and please tell me if I'm wrong—as this solvent recovery step like how you're driving that, I think and if that's the proper interpretation. This is a heat pump. There's like a million ways to do like a solvent-recovery step, a distillations process, a refrigeration cycle. Like there's a lot of different ways to drive this, and we're looking at a lot of them for our system. And I'm sure it's going to vary between what solvent someone is using in these processes so yeah, that's definitely a possibility if I interpreted the question correctly.

>>*Deb Agarwal:*   Thanks and, you know, I'll apologize. I mean I'm reading these questions off. Thank you to the audience for such great questions. We do highly recommend that you reach out to Aaron if you have additional questions that you'd like answered or, Leon, for your question if we didn't get it right. Please feel free to reach out to Aaron. Aaron, do you have your email address on a slide so we can put that up?

>>*Aaron Wilson:*   I do not. I do not in fact. Maybe, no, no, I take that back. No, I actually don't. It's Aaron.Wilson@INL.gov so …

>>*Deb Agarwal:*   Okay, that's easy enough so Aaron.Wilson@INL.gov?

>>*Aaron Wilson:*   Yeah, I'll type it in down here.

>>*Deb Agarwal:*   Yeah, I was going to just do that. Make sure you set your Send to Everyone so that it goes out, yeah. So thank you so much, Aaron. This has been fantastic seminar. Learned a lot of chemistry with this and a lot about what you can do in terms of precipitates. And I'm sure you'll get lots more questions, but we really appreciate you coming and giving this seminar.

>>*Aaron Wilson:*   Yeah, yeah, no, no. I totally appreciate it and I really appreciate the questions. And I realize that I'm not presenting a conventional theory here, and I realize I skipped out on kind of comparing it and contrasting it with electrostatic theory, which I'm well aware of. And it's just I didn't want to start with a criticism of electrostatic theory. So I wanted to present the value of this approach and then maybe somewhere along the line we can do a compare and contrast. So but I would love to hear from everyone with a really rigorous grounding in that field so to learn more. I mean with COVID and stuff it's hard to – there aren't meetings to really exchange ideas at. So this is as close as we get as well as the unconference coming up tomorrow and the next day. So, yeah, please reach out. I would love to talk offline. And I'm perfectly happy to be told that I'm doing it completely wrong so … *[laughs]*

>>Deb Agarwal: *[Laughs]* Thanks, Aaron. No, I think this is pretty exciting, so I'm going to bet you're going to get lots of good questions. And thank you all to the audience for joining and for all the great questions. Sorry we weren't able to let you ask them all yourselves. But, hopefully, I represented them well enough that we got good answers on everything. And I think with that, I want to close things out and, again, thank you, Aaron, for the wonderful presentation. And we don't yet have the June modeling webinar in the NOWEE webinar series set up. But we will mail that out as soon as we plan that out.

Please, if you're interested in presenting in this seminar series, please reach out and let us know. And we'd be happy to schedule you into a slot. All right, thanks everybody. Bye-bye.

[End of Audio]