CERAMIC TECH CHAT

Episode 42

Title - "Innovative solutions for low-carbon cement: Shiho Kawashima (E42)"

INTRO

McDonald: "I'm Lisa McDonald, and this is Ceramic Tech Chat.

With global demand for cement continuing to rise, there is a similarly increasing focus on the material's carbon footprint. As such, players in the cement and concrete sectors are working diligently to achieve a reduction in emissions, such as by adopting new processing methods and laying out clear guidelines and regulations for the industry.

Some may wonder how the industry can innovate such a seemingly dull material. But researchers who work on cementitious materials know that concrete is anything but a static, unchanging system."

- Kawashima: "Concrete's an incredibly interesting, complex material system. It's a material that is continuously evolving. There's a lot more that we can do in terms of more sustainable practices."
- McDonald: "That's Shiho Kawashima, associate professor of civil engineering and engineering mechanics at Columbia University in New York. She studies the flow, or rheology, of cementitious materials, which is a key property in developing new compositions for concrete used in commercial applications.

In today's episode, Shiho will identify the main culprits behind high carbon emissions in the cement and concrete industry and describe the role her research plays in innovating solutions to this challenge."

(music)

SECTION 1

- McDonald: "So for our listeners who may not be that familiar with cement and concrete, can you describe the difference between cement and then concrete?"
- Kawashima: "I am so happy you asked me that question, Lisa, because I feel like it's my responsibility as a cement researcher to clarify that. Because a lot of folks use it interchangeably, which is understandable. But concrete is a composite system, and volumetrically it's mostly fine aggregate and coarse aggregate. So sand and rock, stone, gravel. But then there's cement and water, and that makes up the binder, the glue that

holds all the other components together. So, cement is a key active ingredient, the gray powder that's used in concrete production.

So, concrete is heterogeneous at all scales. So, it has a nanostructure, microstructure that will directly impact its performance. So it impacts its mechanical properties, durability.

But it's also a material that is not static. So as soon as cement and water interact, it undergoes a series of complex chemical reactions. It first starts off as kind of a highly deformable, kind of flowable material. But then within a few hours it sets, and it goes from a few pascal strength to tens of megapascal strength, all under ambient conditions.

So, concrete doesn't gain strength by drying. It actually needs water. It gains strength through a hydration reaction."

McDonald: "That I think is really key because a lot of people, you just think, 'Oh, it's drying.' But it's actually an underlying reaction taking place there."

Kawashima: "There you go."

- McDonald: "So, I know that there's been a lot of talk in recent years around cement and concrete and the carbon emissions that come out of the sector. So can you tell us a little bit about where these carbon emissions are coming from—from both the cement side, just the processing of the cement—and then potentially after, where we have the concrete, we're going to use it, how that can lead to carbon emissions."
- Kawashima: "Yeah, that's a really great question. So, most of the carbon emission associated with concrete is tied to the production of cement. And so although cement makes up about 10% to 15% of concrete by volume, it accounts for nearly 90% of its emissions. So, it's really the cement that is the reason behind the high emissions of concrete.

So why is the production of cement so carbon intensive? And one of the main reasons is that we use limestone as a raw material. It's a key feedstock material. And limestone is calcium carbonate. So it's a carbon-containing material. And we use it as a calcium source, a calcium oxide source, for cement production. And so in order to get that calcium, we burn it. So we calcine limestone, and that calcium oxide is used for cement, and the CO₂ is just directly emitted into the atmosphere. And so there are direct emissions associated with calcination of limestone.

And then there are also indirect emissions for the heating process. The burning of fossil fuels to heat cement kilns. And so we put the raw materials, which is limestone and some source of silica, into these massive cement kilns, and then we burn them at temperatures of up to 1,450°C.

And so, the carbon intensity of the process itself and combine that with just the mass amount of cement that we produce globally—so this is billions of tons per year—that leads to the cement sector, accounting for the number, there's a range, but 5% to 8% of anthropogenic CO₂ emissions globally.

So, there's other kinds of emissions in the process, but that really is the main one."

- McDonald: "Luckily, though, like you said, concrete is a composite material. And so there's different ways that we can lower that emissions by maybe potentially finding different things that we can put into the concrete to lower the cement amount or even different cement compositions. Right?"
- Kawashima: "Yeah, that's right. So I think that's such an important area. And I know the cement community is really focused on these efforts now. And so there's a lot of different pathways towards decarbonizing the cement sector.

On the materials side, there are things that we can do now. Like you mentioned, we can find replacement materials for cement. So this includes what we call supplementary cementitious materials, or SCMs. So that includes coal fly ash, slag. And again, these are already used by the industry. They're in the code and the standards. And we can also use fillers, like limestone fillers. So the same limestone that we use as a raw ingredient for Portland cement production, but we don't calcine it, right? We just grind it into a powder and use it directly.

And so this is already done. But we can kind of be more aggressive with the replacement levels to further reduce the cement content.

And we can also explore, as an additional direction, there's work being done on utilizing more diverse waste streams. So again, currently, we're really reliant on fly ash, which is a byproduct of coal combustion. But hopefully that supply goes down as we decrease our reliance on fossil fuels. But then we have to kind of figure out alternative sources for SCMs. And so that can include more diverse industrial waste streams.

And there's really interesting work that we are also part of, too, where you can use byproducts of CO_2 mineralization schemes. So in CO_2 mineralization, you can potentially take industrially emitted CO_2 in a gaseous form and then convert them into solid carbonates, which can then be used as fillers to replace cement. They can also be used to serve as synthetic aggregate to replace natural aggregate. And so the benefits of that are twofold, right? So you can use it as a filler to reduce cement content, but then you're also, it's essentially a permanent storage source of CO_2 .

And so that's one thing, replacing cement content. But there's also work being done in coming up with alternative production of Portland cement. So instead of calcination, the way we do things now, burning it, can we leverage electrochemistry pathways to still extract that calcium but then make it carbon neutral by reintroducing that CO₂ and eliminating the thermal emissions. And the benefit there is that the end product is still Portland cement, what the industry is used to.

So further is just completely different binder chemistries altogether. So replacing cement as we know it with completely different types. So we use calcium-based cements. There's magnesium-based cements, acid-based cements. But that would really shake things up a bit because it'll be very different. It's going to be a completely different chemistry, require completely different infrastructure. But if we want to achieve neutrality or negativity, I think that's going to be a necessary step."

(music)

SECTION 2

- McDonald: "Using these different materials, using these different fillers is going to turn things upside down a little bit because the cement is now going to have slightly different properties than the traditional compositions that we have been using. And you work a lot in this space, about looking at the properties of cement-based systems. So can you talk to us a little bit about like what types of properties you look at and some of the different cement-based systems that you've been exploring?"
- Kawashima: "Sure. Our lab, I would say, we really focus on early-stage properties. So that includes the flow behavior, or rheology. And we're interested in rheology because although it makes up a very short time period of the life of concrete, it's really important for constructability. You can design the most high-performing or most sustainable concrete, but if you can't cast it, then you can't use it.

And so for us, whenever we are investigating a new material, we do comprehensive rheological characterization to see if there are any issues and then find ways to kind of mitigate those issues. But also look at potential beneficial effects or behaviors that can be leveraged to make certain casting approaches more efficient or even make new casting approaches possible.

And so, one project I'm working on is with professor Alissa Park. She was at Columbia, now she's at UCLA [University of California, Los Angeles] as the dean. But she is an expert in energy and materials conversion, including carbon capture, utilization, and storage schemes. And our project was on upcycling demolished concrete waste, and specifically focusing on the paste phase, because that's the part that's rich in calcium and silica, the kinds of things that we like to use in concrete and cement.

And so she has this extraction and CO_2 mineralization process. Basically she extracts calcium from this waste cement and then applies carbonation, is able to form these solid calcium carbonate particles. And then the cool thing is there's this silica-rich residue that can also be used as SCM. So you have this solid carbonate that can be used as a filler and a silica-rich material that can be used as an SCM. And both can be used to replace cement for concrete production.

In this project, the cool thing about these advanced CO₂ mineralization schemes is that you can start to produce different polymorphs. So calcium carbonate has different

polymorphs: calcite, vaterite, and aragonite. Calcite is the most stable form, and so that's the form that is found very prevalently in nature. And that's the kind of calcium carbonate that we use in industry, including the concrete industry. But there are these two other polymorphs, these metastable polymorphs, aragonite and vaterite, which aren't naturally occurring really in nature because they're metastable. But they can be formed using these mineralization schemes.

And the cool thing is that they exhibit very distinct morphology. So calcite is kind of cubic, aragonite is needle-like, and vaterite is spherical and a little porous. And that can point to very different effects on not only rheology but hydration kinetics, setting behavior, strength gain, mechanical properties, durability. So, we are exploring all of that, and we're already seeing these very distinct effects of the different polymorphs. Although they're all calcium carbonate, because they are all quite different in morphology, they impact cement hydration very differently.

And very interestingly, on rheology, the aragonite in particular, because they're needlelike, they have a high specific surface area, we're seeing very, very distinct behavior where it enhances a property called thixotropy. And basically, it's kind of like ketchup. So, ketchup is a thixotropic material. And so what do I mean by that? It's a fluid or suspension that can undergo sheer thinning or structural breakdown when agitated or subjected to shear. But then once it's at rest, it's able to recover that structure or exhibit structural rebuilding.

So ketchup, you know, if you're using like a glass bottle and you flip it over, nothing happens, right? We have to kind of bang on it. You have to agitate it a little bit. And then it starts to flow. And if you look at it, it actually starts to flow faster and faster, and that's the sheer thinning behavior. But then, if you put it down and you use it again, it's not going to just flow, right? You have to kind of go through the same process of agitation. So that means that it exhibited structural buildup while it was at rest.

And cement-based materials also exhibit this behavior. We found that aragonite in particular helped with the structural buildup aspect. It led to higher what we call yield stress, the stress needed to initiate flow, and a faster rate of increase of yield stress. And that was interesting to us because, this might be a segue to like the next thing kind of, but thixotropy, that shear thinning and structural buildup behavior, can be leveraged for 3D printing applications.

So those are the kinds of things that we do."

McDonald: "Well, that did just make the perfect transition to the next part that we want to talk about, which is there's some new emerging sectors, such as 3D printing in construction, that are coming up as like new ways that we can maybe make the cement and concrete industry more sustainable. So can we talk a little bit about how creating cement-based systems for 3D printing is maybe different than creating them for traditional casting systems?" Kawashima: "Yes, absolutely. So kind of just to explain what it is for folks that aren't familiar. So, starting with conventional formwork casting of concrete. So the way that we cast concrete and the way we have cast concrete forever is through the use of formwork. So first you construct the formwork, and then you cast or pour your concrete into that formwork. And then once your concrete has developed sufficient structure and strength, then you can strip the form work. And that's your final structure or structural element.

With 3D printing, you eliminate the need for formwork altogether. And so once you eliminate that big step of constructing and stripping formwork, it leads to significant increase in efficiency in terms of time, material, labor.

And so, tied to labor, another feature of this is that it's automated, right? So it's done by robots. And there is a skilled worker shortage in construction, where currently the needs of construction outweigh the availability of a skilled workforce. And so it can address those needs.

And so, in addition to kind of the overall increase in efficiency, if it's executed properly, is the aesthetic freedom, the flexibility and form. So with conventional formwork casting, you have to be able to build the formwork first to achieve whatever form you want. And the cost and labor scales with the complexity of the structure when it comes to formwork construction. But with 3D printing, no matter how complex the structure is, the costs and the time can remain constant, right? Because you're just directly depositing the material. So that points to again a lot of opportunities in terms of design freedom, but also you can start to leverage optimization schemes. So only deposit material where it's necessary. So that can help with reducing material requirements as well.

Yeah. And so, it's a technology that's still very much under development. It is so different from the way we've constructed thus far. But there are startups that are already 3D printing homes. So it's happening.

And there's definitely early use cases that I can see. So rapid construction, disaster relief. It enables remote construction. But I think the main one is going to be just leveraging that design freedom that you can achieve with 3D printing."

- McDonald: "If I remember right, I think my coworkers told me that at a previous Cements Division meeting, some students used it to create a 3D-printed aardvark or anteater."
- Kawashima: "Oh, my goodness, that's right! So I remember that. That was at UC Irvine, ACerS Cements 2022. And they have some great printing capabilities there. And yeah, they printed like an aardvark. I guess that must be their mascot. And they had everyone sign it. Yeah, right."

McDonald: "It's a great example of design freedom that this technology brings to you."

Kawashima: "Absolutely."

- McDonald: "In addition to 3D printing, I know that you've also had some experience with the emerging field of nanoparticle modification of cements. Are you able to talk a little bit about your work in that area?"
- Kawashima: "Sure. So it ties to 3D printing, actually. My Ph.D. work was mainly on the use of nanomaterials. And specifically, I was really interested in nanoclays and the impact of nanoclays on fresh-state properties. So my Ph.D. really set me up really well for 3D printing, I have to say.

So nanomaterials are considered to be materials that have at least one dimension at the nanoscale. Because of their fine size, they have very high specific surface area, and that really can lead to very enhanced effects. So, for example, clays. When you incorporate some clays into cement-based materials, clays themselves are thixotropic systems, and we already all know what thixotropy is, right? And so when you add clays into cement-based materials, that leads to more enhanced sheer thinning and structural recovery. But then we found that when you use nanoclays, then they have an even more enhanced effect. So more significant sheer thinning, more rapid structural buildup. And it really is tied to their dimension. Where you have a more enhanced effect, but then you can use much less of the material.

But that's just one example. So, you know, silica fume is also a material that's used in cement-based materials. It's a relatively reactive material. But if you utilize nanosilica, then they can have these very enhanced effects on cement hydration, they can significantly enhance cement hydration kinetics, and even lead to enhance pozzolanic reactivity.

So basically, nanomaterials are this interesting technology where if they're processed correctly, then at very small addition, they can have very, very dramatic effects. Yeah."

(music)

BREAK

McDonald: "The American Ceramic Society's Cements Division is involved with the research, development, manufacture, and sale of cements, limes, and plasters. This Division organizes the Advances in Cement-Based Materials meeting each summer. Learn more about this Division at www.ceramics.org/cementsdivision."

SECTION 3

- McDonald: "So, what was your pathway to becoming involved in cement and concrete research?"
- Kawashima: "So, it wasn't much of a pathway. It kind of all happened in one day, where I decided to do this. So when I was an undergrad, I studied civil engineering and actually did my undergraduate here at Columbia. And at the time, I just wanted to be a structural engineer, like a forensic structural engineer. But then I just decided that maybe that wasn't

the right path for me. So then I decided to kind of pursue master's degree. And so, when I was starting to explore the idea of going to grad school, Northwestern kind of was always a school that I was interested in. So I went to Northwestern for a visit.

They were really great about putting together like a schedule for me. And I can't quite remember all the groups that I met. I remember one, and that was professor Surendra Shah's group. And professor Surendra Shah, he's kind of one of the most renowned cement researchers in the world. And of course I didn't know that at all at the time. But I had this meeting with him, and he just started talking to me about cement-based materials, and he told me about the research that goes into cement-based materials. And it kind of blew my mind because I didn't even know that you could study concrete as, you know, a field. But he somehow was able to kind of hook me in, and I also then met with many of his Ph.D. students, and they showed me around the labs, and I saw like an SEM [scanning electron microscope]. And it was just, I just thought it was really amazing.

And so I remember talking to my mom. And I was like, 'Well, instead of that one-year master's program, I think I'm just going to exclusively apply to Ph.D. programs. And that's going to be like a 6-to-7-year commitment. And I think I'm going to study cement.' And it was really just that day I decided to just go for it. And luckily I was able to get into Northwestern, and I was able to work with Professor Shah. But really it was Professor Shah and his group that really got me into it. And I'm just really thankful for that even today."

McDonald: "He cemented a very good foundation."

Kawashima: "Yes, he definitely did."

- McDonald: "So, I know you've been a really involved member of ACerS. You've served as past president of the Cements Division. So can you tell us how you came to become a member of ACerS?"
- Kawashima: "I love ACerS, I really do. It's not because I'm on an ACerS podcast right now. So, how did I become involved? So, part of the ACerS Cements Division specifically, and the main thing that the Cements Division does is hold its annual meeting, the Advanced Cement-Based Materials meeting. And I attended my first one my first year as a faculty member. So in 2013. And it was at...it was either at UIUC [University of Illinois Urbana-Champaign] or Northwestern. But that was my first meeting, and I loved it because it's a relatively small meeting for us. It's about 120 people in total who are in attendance. And that might seem small, but all the people you want to be talking to and all the people you want to know within cements with a focus on the materials science aspect, the fundamental understanding, they are all there.

And so that's why I realized at the first meeting, and the meeting is small enough where, even if you're like shy or introverted, it's a very nice setting to actually introduce yourself and talk to these people, to everyone. And, yeah. I think ACerS is the main way I got to know my community. Specifically, folks who work on cement science. And so ever since

that first year, I don't think I missed any meetings. I think just one when I was having my kids.

And yeah, I, you know, again, it's a small community, and I got to know the people in the community, and I was lucky enough that I was invited to serve on the executive board. And I just attended my last meeting, I think, last week on that board, and I was a little sad. But the current board is just awesome. So Wil Srubar at UC Boulder [University of Colorado Boulder] is now the chair, and he's just great. And the board is just full of really enthusiastic people. And I think they're really excited about putting on more events like webinars, or some things like between the annual meetings, which is always great. But just some things that can be held between the meetings, with a focus on students and young professionals.

So again, yeah, there's really just a sense of community there. And I chaired the last meeting, which was this past summer in June. And I co-chaired it with Dimitri Feys of Missouri S&T, who's also just awesome to work with. And it was very stressful, but it went relatively smoothly. And I would say it was like one of the highlights of my professional career. It was nice to be able to give back. So, yeah, just all good memories there."

(music)

CONCLUSION

McDonald: "The ubiquity of concrete in today's built environment means we often take this composite material for granted. But the cements that give concrete its properties are constantly evolving to help realize a sustainable world."

I'm Lisa McDonald, and this is Ceramic Tech Chat."

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"Visit our website at ceramics.org for this episode's show notes and to learn more about Shiho Kawashima and her research. Ceramic Tech Chat is produced by Lisa McDonald and copyrighted by The American Ceramic Society.

Until next time, I'm Lisa McDonald, and thank you for joining us."