
Cold mix design: A rational approach based on the current understanding of the breaking of bituminous emulsions

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ABSTRACT: The general environmental concern all over Europe constitutes a strong incentive towards cold technologies and therefore designing cold mixes with bituminous emulsion has become a key subject in the last few years.

However, cold mix design is not an easy task and necessitates first a good knowledge of the physicochemical aspects involved in cold mix properties, from the characterization of the emulsions to the final application with a given aggregate.

Therefore, this paper presents an up-to-date description of the chemistry and physics of bituminous emulsions and their interactions with mineral matter, based on recent published results. In particular, the key parameters involved in the breaking process are highlighted. From this overall picture, a general method to design cold mixes is proposed. This highlights the work needed in terms of testing and standardization in order to develop a rational mix design method, without which further development of cold technologies will be difficult.

KEY WORDS: Emulsions; Cold Asphalt; Mixture Design; Testing; Formulation;

1. Introduction

Cold technologies are generally regarded as Environmentally Friendly Construction Technologies (EFCT) because they help reduce energy spending thanks to the use of wet aggregates and lower operating temperatures, diminish fume and particles emissions to the atmosphere and therefore limit the impact on the environment. In the present environmental context, such technologies surely sound highly promising and this is materialized by the current endeavour towards cold mix techniques, as exemplified by European research efforts such as the former OPTEL project [ECK 01] or the on-going SCORE project [LES 04], or by the organization of big events such as the now 10-years old World Congress on Emulsions which gathers, among others, bitumen emulsion technologists.

However, and in the eyes of the end-users, cold mixes remain highly technical materials and therefore are thought to present some kind of technical risk. Therefore, they are essentially used in a very narrow application range on mostly secondary roads. For example, Gravel-Emulsion is essentially used in France for reinforcement and reprofiling when its good fatigue resistance could make it a very interesting material even for new constructions [LES 02]. The situation is looking somewhat brighter in the case of microsurfacing, which constitute a very specific type of cold mixes used on occasion under high traffic levels, for example in Spain, but they however are far from representing the typical solution for wearing courses for highly trafficked roads.

One way to improve the use of cold mixes would be through standardization of their design, giving the end-users a much clearer estimate about the quality of the materials than current specifications or practices do. Hence, this article tries to present the key stages that are needed in a rational design method based on the current understanding of the breaking of the emulsion. With a tight control of all these aspects at the design level, we are quite certain that cold mix quality will increase together with the confidence of the overall profession in their possibilities.

Thus, this paper first reviews our current knowledge of the breaking of bitumen emulsion in the presence of mineral matter from which we highlight the critical steps which should be included in any mix design procedure. This allows us to discuss the available test methods for each critical step and give some guidelines for the future research that is needed in order to help develop cold technologies.

2. The breaking of bitumen emulsions

2.1. Bitumen Emulsion Stability: Definitions

In order to understand the breaking of bitumen emulsions, it is necessary to define precisely what is meant by “breaking”. In this article, the breaking of the emulsion represents the sum of all the events leading to the transformation of the initial bitumen emulsion to a final film of bitumen. Coalescence is then defined as that specific step of the breaking process where individual droplets of bitumen merge to form larger drops, as will be described in more details later on. This definitions for breaking and coalescence are in line with their accepted meaning by the International Union of Pure and Applied Chemistry [EVE 72].

In order that the emulsion breaks, it has to be somewhat unstable so that the initial droplets of bitumen have a restricted life time and tend to coalesce. However, the notion of stability must be clearly defined as well.

In the current sense, the stability of the emulsion is either related to its ability to withstand sedimentation or to its breaking behaviour. For example, current Spanish [DGC 00] and French [AFN 84] specifications define an emulsion “stable” as regards sedimentation when the upper part of a vertically stored bitumen emulsion do not contain less than a 5 % difference in bitumen content than the lower part after 7 or 15 days storage respectively [AFN 83,AEN 99]. However, the physical meaning of this test has little to do with the stability toward coalescence, and it rather relates to the particle size of the emulsion through the sedimentation rate described by the celebrated Stokes equation [TAD 83,SFE 88].

The stability of slow-setting emulsions is also evaluated by means of the stability towards cement test in both Spanish and French specifications [AFN 84b,AEN 98]. In this test, the physicochemical stability is evaluated since the breaking behaviours of the emulsion is clearly quantified by the quantity of broken emulsion when mixed with cement. In this test, the breaking is materialized by the fact that the broken emulsion can not be washed away by water.

This corresponds exactly to what is meant in this article by stability: an emulsion is said to be stable when the droplets retain their individuality as opposed to an unstable emulsion where the droplets tend to coalesce to form a final film of bitumen.

2.2. Bitumen Emulsion Stability: A Theoretical Basis

On a physicochemical standpoint, emulsion stability is obtained thanks to the repulsive forces between bitumen droplets. These interparticle forces can be described by the so-called DLVO theory, named after its founders Derjaguin-Landau-Verwey-Overbeek [ISR 92]. According to this theory, inter-droplet interactions are the sum of an electrostatic repulsion and a Van-der-Waals attraction. When the repulsion overcomes the attraction, the droplets are prevented from approaching each other and the emulsion is stable, i.e., no breaking occurs. On the opposite, when the attraction overcomes the repulsion, the droplets tend to contact

and then coalesce.

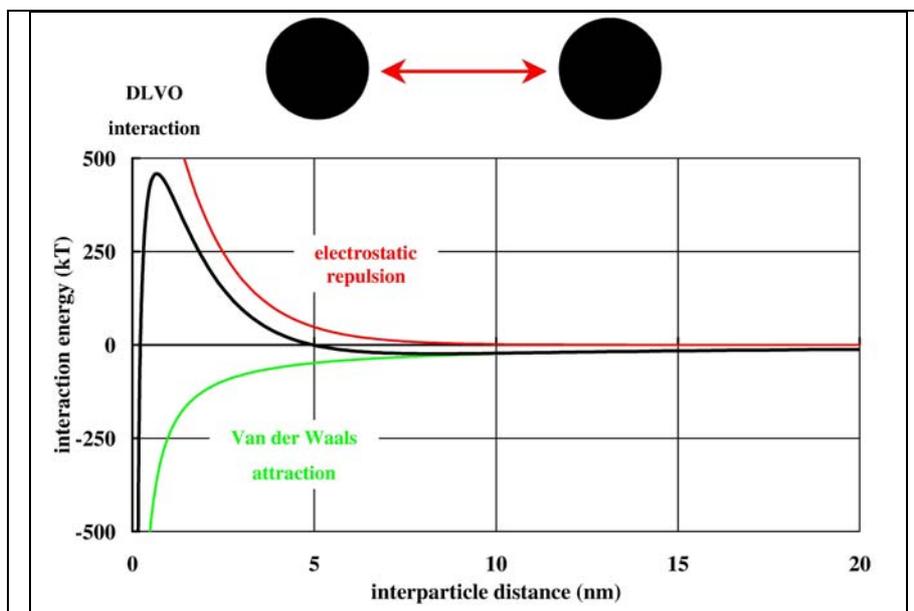


Figure 1. Typical DLVO interaction between two bitumen droplets and its two main electrostatic and Van der Waals components: interaction energy (in units of thermal energy kT) versus interparticle distance.

The fact that DLVO theory explains emulsion stability has been demonstrated [TAK 87], although a minor part of the interaction forces might come from non-DLVO interactions, that is other than electrostatic or Van der Waals forces [LAR 02, ROD 03]. Even so the detailed mathematical treatment of these phenomena fall outside of the scope of this paper (see [ROD 03] for a review), an example of a typical DLVO interaction between bitumen droplets is given in Figure 1. Since these energies are quite low, a convenient unit to express them is using thermal energy units of kT , where $k = 1.38 \cdot 10^{-23} \text{J/K}$ is the Boltzmann constant and T the absolute temperature. At room temperature (20°C), $kT = 4.05 \cdot 10^{-11} \text{J}$.

Note that in the typical case described in Figure 1, a weak minimum of order $-20kT$ is observed for a distance of 8 nm, which induces a weak flocculation of the emulsion and is probably at the origin of the very low yield stress observed in their flow curves [LES 03b]. It could be even deeper generating higher yield stress if the emulsifier content is increased thanks to non-DLVO depletion interactions [LES 03b].

The Van der Waals attraction is a macroscopic manifestation of the intermolecular attraction between like molecules [ISR 92]. A typical energy versus interparticle distance for this attraction in the case of bitumen droplets is also pictured in Figure 1. This component depends on the chemical composition of the bitumen at hand and can be thought to be constant regardless of bitumen origin in a first approximation [ROD 03]. Therefore, this clearly means that the formulator has no choice but to deal with this attraction between bitumen droplets.

On the other hand, the electrostatic repulsive interaction comes from the presence of electrical charges on the droplet surfaces and arises because like charges repel each other. In our case, these charges are essentially those coming from the polar heads of the emulsifiers. The total charge on the droplet surface can be estimated through zeta-potential [TAK 87,ROD 03]. A typical energy versus interparticle distance for this repulsion is pictured in Figure 1 for the case of a zeta-potential of 100 mV. It can be also calculated from the emulsifier structure knowing its surface concentration (for example through adsorption isotherms [VAN 01]). However, quantifying the surface charge is not enough to compute the full repulsive interactions, because their precise evolution versus inter-particle distance depends also on the ionic strength, that is the presence and quantity of all ions in the medium.

The formulator indeed controls this part of the droplet interactions by first choosing the type of surfactant and its concentration, together with its ionic environment (pH, salts,...). The nature of the bitumen will also have some influence, since charged species might migrate to the interface, therefore changing surface charge [DUR 77].

Given this context, the breaking of the emulsion is a consequence of the diminution of the surface charge up to a point where it can not overcome the Van der Waals attraction anymore. Therefore, controlling the breaking of the emulsion amounts to controlling the way the surface charges of the droplets evolve in a given environment. This can be done by removing part of the emulsifying agent, by neutralizing its charge,...

This picture represents the case where a bitumen emulsion is brought into contact with some specie (cement, aggregate,...) modifying directly or indirectly the surface charge of the droplets and/or their ionic environment, therefore inducing breaking. However, another route can be followed to cause the emulsion to break, which consists in removing the water from the emulsion – for example through evaporation - so that only the bitumen remains [BOU 96]. In this case, breaking occurs when bitumen concentration becomes so high that the droplets are pushed against one another, the crowding finally overcoming all repulsive forces. Note that bitumen emulsions can be sometimes so stable that crowding do not lead to breaking unless the bitumen concentration exceeds 98 %. As will be detailed hereafter, this scenario is indeed sometimes used in cold mixes and leads to a very different breaking behaviour, which is similar to what currently done in the field of latexes for paints [KED 97].

Hence, the breaking of the emulsion can now be described in rational terms as a consequence of two causes:

- Disappearance of the electrostatic repulsion between droplets (gel contraction),
- Very high bitumen concentration (film forming).

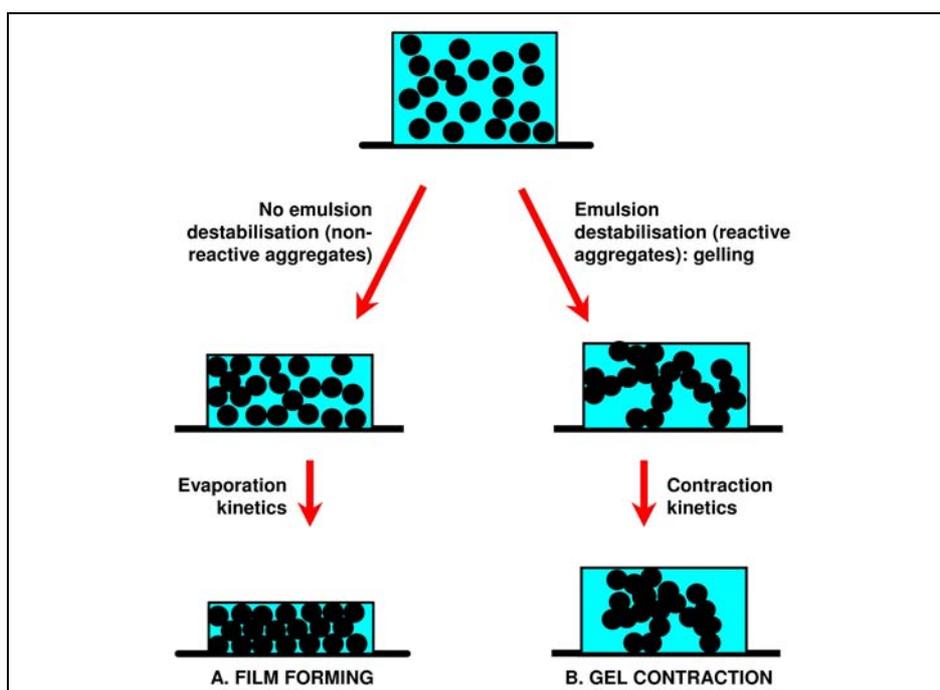


Figure 2. The two possible breaking scenarios for the bitumen emulsion in contact with mineral aggregates.

2.3. Breaking of the Emulsion by Gel Contraction

When the breaking of the emulsion is obtained through the disappearance of the electrostatic repulsion between droplets, it has been shown that the kinetics is then very rapid and that once the repulsive barrier disappears, the droplets form an initially loose gel which then starts to contract in order to limit the contact area between bitumen and water ([BON 01] - Figure 2B). The characteristic time τ_c for the contraction kinetics is a function of the viscosity of the bitumen η , the bitumen

droplet size a and the interfacial tension γ between the bitumen and the water [PLA 02]:

$$\tau_c = \frac{\eta a}{\gamma} \quad (1)$$

Therefore, if the breaking mode follows these lines, bitumen viscosity and thus paving grade will be of importance, as well as particle size and interfacial tension. If the first two parameters can be measured without much difficulties - although measuring bitumen viscosity at room temperature might be quite tricky - measuring the interfacial tension surely is not an easy task [ECK 01b]. If measuring these parameters is not necessary at the level of the mix design, it still gives some clues about the ways the kinetics can be changed. For example, the use of fluxed bitumens allows for a decrease in the viscosity and hence for an increase of the contraction kinetics.

In general, this breaking mode is activated by the action of the aggregates or of an additive such as Portland cement or lime. In fact, slow-setting emulsions are commonly manufactured with fatty polyamine surfactant, that have a peculiar behaviour as a function of pH [BOU 96]. More precisely, these cationic surfactants only possess a net charge when put in an acidic medium, due to the binding of protons from the acid to the amine groups. When put in a neutral or basic environment, the amine groups lose their additional protons and hence their positive charges. At the bitumen droplet level, the electrostatic repulsive force then disappear once the pH increases. Therefore, changing the pH is one very efficient way to induce the breaking of emulsions made with these surfactants.

In a cold mix, the pH increase can be induced by the aggregate, depending on its petrographic nature [ECK 01c,LES 03,BOU 98]. This corresponds to a so-called "reactive" aggregates, example of which are not only limestone but also some alumino-silicates aggregates [ECK 01c,LES 03]. On the opposite, other aggregate barely have an effect on the pH of the aqueous phase of the cold mix and therefore do not break the emulsion [ECK 01c,LES 03].

In parallel to this change in pH, cations are released from the mineral surface, primarily calcium ions at concentrations up to 1 g/l [LES 03], but also magnesium, etc., which can induce precipitation of the emulsifiers in some cases, and in all cases, a destabilization of the emulsion due to an increased ionic strength. Note that the water quality of aggregates in their natural humidity is somewhat different from that of aggregates that are just brought in contact with the added water. In the former case, the ionic exchanges already have taken place long before introducing the emulsion, whereas they occur only when in contact with the emulsion in the latter case [LES 03]. This will have an influence on the overall ionic content which is generally higher in the first case.

In all cases, the second kinetic effect will come from the time needed for the ionic environment to change up to the point where the emulsion becomes unstable. Ingenious ways to measure this induction time by electrodeposition were described

by M. Bourel [BOU 02]. Typical time for such event is of order of 5 to 30 min from pH increase test, but will in fact be a function of aggregate nature, quantity and surface area [BOU 98,ECK 01c,LES 03]. To a lesser extent, the emulsion formulation will also play a role, for example through the emulsifier nature and content [ECK 01c, DEL 02,LES 03].

Therefore, the overall breaking time will be the sum of this induction time plus the contraction time.

2.4. Breaking of the Emulsion by Film Forming

If the emulsion is now broken as a consequence of water evaporation, the breaking follows the general scenario which is well known for latexes [KED 97] and that can be named "film forming". The droplets retain their identity up to a very high concentration, which can be higher than 98% for slow-setting bitumen emulsions (Figure 2A). From then on, the crowding pressure becomes high enough to generate the breaking of the water films between the bitumen droplets and hence, to induce coalescence.

The kinetics of the film formation is then imposed by the evaporation rate, which can be quite slow under some European climates. Evaporation can even stop or worst, rain can fall, so that the overall process is completely arrested if not delayed. In other words, this route can be very dangerous if the cold mix layer is not protected by some waterproof coating, which in turn, might slow down the evaporation process.

An interesting feature of this breaking scenario, is that the concentrated emulsion starts to have mechanical properties close to that of the final bitumen film as soon as close packing of the bitumen droplets is obtained [LES 01], that is close to 75% bitumen for conventional bitumen emulsions [LES 01b]. In general, this concentration will be a function of the overall particle size distribution. Therefore, all water do not have to evaporate to give acceptable final properties.

Still, the closely packed emulsion remains an emulsion, which means that the bitumen droplet would redisperse when more water is added. Therefore, if this breaking solution is chosen, there is a risk that the emulsion do not really break but remains in this reversible highly-concentrated state.

2.5. Aggregate/Emulsion Adhesion

In parallel to the breaking of the emulsion, part of the droplets will cover the aggregate surface providing that the aggregate/droplet interactions are favourable. This process controls the coating quality.

The droplet attraction by the aggregate surface is generally thought to be of electrostatic origin and therefore depends on the aggregate surface charge, and hence on its petrography, and on the droplet surface charge [SFE 88,BOU 98,DEN 02]. For example, siliceous aggregates are said to bear negative charges and therefore attract all positively charged droplets. Still, there is a competition in the adsorption of the free emulsifier from the emulsion and the bitumen droplets. Due to their much bigger micron size, the droplets are however much slower and therefore surfactant adsorption is the fastest process [BOU 93]. Note that droplet size will influence the process since the larger the droplets, the slower they diffuse. Therefore, the formulator has to control the amount of residual emulsifier in order to change the number of surface sites available for the droplets. Here, the “free”, “non-adsorbed” or “residual” emulsifier is that part of the emulsifying agent which is not located at the bitumen-water interface and therefore remains in the continuous aqueous phase of the emulsion [VER 01].

Also, an excess of surfactant is dangerous not only because it will not leave any surface available for the droplets, but also because it can form a repulsive double layer on the aggregate surface when in excess [BOU 96].

In parallel, the formulator has to choose the right surfactant in order to have a lasting favourable bitumen/aggregate adhesion which in theory depends on the aggregate type, but in practice, was found to be quite acceptable with most fatty amine type surfactants and their derivatives [SFE 88,SAL 97].

The modifications of the mineral surface following the desorption of cations described in a previous section, causes a competition between the re-adsorption of the cations and that of the emulsifier. This can for example be easily studied by the simple flotation test, which combines surfactant adsorption and cations desorption [BOU 98].

Once the formulation is well chosen from the above analysis, the droplet has then to deform so that the bitumen completely wets the surface. This process can be quite slow and is known to be a function of the viscosity of the bitumen η , the interfacial tension γ between the bitumen and the aqueous phase and the dynamic contact angle θ between the bitumen and the aggregate surface in water [DEG 85]. Assuming that the presence of surfactant generates conditions of complete wetting for the bitumen, the spreading velocity U , representing the time variation of the radius R of the wetted area is:

$$U = \frac{dR}{dt} = \frac{\gamma}{\eta} \theta^3 \quad (2)$$

Therefore, if the quality of coating will be governed by the emulsifier choice, its kinetics will be a function of bitumen viscosity and the details of the aggregate/bitumen surface properties through their contact angle in water, which in turn is affected by the quantity and nature of emulsifier.

Note that recent work suggests that the emulsion droplets can be too big to

access the mineral surface at early mixing stage in the case of rapid breaking [BAR 02]. More precisely, the water added prior to the emulsion introduction can remain in the form of thick capillary films around the mineral filler with no intimate mixing with the emulsion, limiting the emulsion-aggregate contact. Therefore, the above adhesion time would only come into play at a later stage when the said water film has disappeared thanks to evaporation. So-called compacting additives are supposed to prevent this phenomenon [BAR 02]. In fact, this difference between the water from the aggregates (added water) and the water from the emulsion was already observed by F. Moutier when studying the compaction of cold mixes [MOU 77].

	Gel Contraction		Film Forming	Adhesion	
	Breaking Kinetics			Breaking Kinetics	Coating Quality
	Induction Kinetics	Contraction Kinetics			
Aggregate	<ul style="list-style-type: none"> – nature (reactivity) – quantity – surface area 			<ul style="list-style-type: none"> – nature – quantity – surface area 	<ul style="list-style-type: none"> – bitumen/aggregate wetting
Emulsion	<ul style="list-style-type: none"> – emulsion quantity – emulsion formulation (emulsifier nature and content,...) 	<ul style="list-style-type: none"> – bitumen viscosity – droplet size – bitumen/water interfacial tension 	<ul style="list-style-type: none"> – bitumen content – particle size distribution 	<ul style="list-style-type: none"> – emulsifier choice and content – droplet size 	<ul style="list-style-type: none"> – bitumen/water interfacial tension – bitumen viscosity
Other Mix Components	<ul style="list-style-type: none"> – total water content 		<ul style="list-style-type: none"> – total water content 		
Other			<ul style="list-style-type: none"> – water evaporation rate 		

Table 1. *The most relevant parameters for the different phenomena.*

2.6. Summary

Finally, the above arguments make it possible to highlight the relevant parameter for each of the individual components of the cold mix for each of the above possible events. Although presented in a slightly different form, the three above phenomena are indeed very similar to the three breaking scenarios already proposed by M. Bourrel and F. Verzaro [BOU 96], namely through adsorption onto the mineral surface, pH increase and water evaporation. Also, if the above picture gives some

idea of the way the final bitumen film forms, it must not be forgotten that the overall process takes place within a wet granular material, which may lead to local water entrapment [BAR 02]. In some extreme cases, with fast evaporation rates, a skin could also form on the surface of a drying microsurfacing, preventing water from evaporating [LES 01,LES 01c]. In all cases, water content in the emulsion is not an indicator of emulsion breaking, except in the extreme case of near zero remaining water.

In conclusion, the above information can be summarized in order to highlight the relevant parameters for each of the events (Table 1). The idea is to list the most significant parameters, keeping in mind that some other properties may have an effect, which will however be secondary in the general case. Temperature do not appear as such, but it strongly influences most of the parameters (bitumen viscosity, evaporation time,...)

3. Practical consequences

3.1. *Properties of the Cold Mix to be Considered*

The above events give the cold mixes a peculiar behaviour, as compared to hot mixes. If a hot mix final in-place properties for a given aggregate gradation and bitumen nature and content, can be easily controlled through compaction and temperature, the situation becomes more complicated in the case of cold mixes.

3.1.1. *Workability*

First, workability of the cold mix, in the sense of its ability to be laid down, is not obtained through a control of the temperature but through a control of the breaking kinetics. As just detailed, this is a process involving a lot of physicochemical factors which can render the task of the formulator quite difficult for some emulsion/aggregate combinations (Table 1). Apart from the formulation aspects, the difficulty also arises from the lack of relevant tests in order to measure it. In fact, workability of the hot mixes is not directly measured as such but can be generally evaluated through relevant indicator from the compaction curve, namely the initial air void content [BAL 92].

For cold mixes, however, it was shown that this indicator does not apply because it barely changes when the emulsion breaks or not [LES 00,BRO 02]. A good alternative is the Nynas workability test [ECK 02], which gives reliable results providing the handling of the cold mix is tightly controlled [DEL 02b]. Still, this test is intended for thick layers and the same has to be done for thin layers such as

microsurfacing. Although the Diason test is a potential candidate [LES 01], there is a need for more research and some other tests currently being developed [BOU 02] or to be developed might be better suited.

3.1.2. *Compactibility*

Then, compactibility in itself has to be evaluated. It is not clear at all at the moment how the above physical parameters do influence the compactibility of cold mixes. The difficulty arises because until now, no laboratory test gives a relevant picture of their in-place density. For example, it is generally observed that whatever the laboratory results, dense cold mixes give a final on-site air void content of order of 15% [LAF 85].

More practically, the best-suited tests to date remain the typical tools for hot mixes, for example the French Gyratory Shear Compactor (PCG). In the case of cold mixes, they need to be equipped with a water sucking device to allow the water content inside the mix to be known at each stage [MOU 77,LES 00]. A recent proposal was to use the PCG, but with different settings, that is 3° angle and 900kPa [POI 98,POI 02] as opposed to the traditional settings for hot mixes (1° and 600kPa). It is however not clear whether this proves realistic, since the compaction can be performed up to total water extrusion from the mix, which is of course never attained in practice. Moreover, this severe loading might generate significant aggregate attrition.

Another proposal using the PCG coming from the results in [LES 00,BRO 02], would be to maintain the traditional settings for load and angle but to change the rotation speed until a realistic point of water extrusion could be found, which would allow to lose about 1% (absolute) water content at a air void content of 15%, values that agree with most field results. From published data, 30rpm could be an appropriate choice. In this sense, compactibility would be evaluated by the number of rotations needed to obtain 15% air voids with 1% of lost water.

In all cases, predicting in-situ density is a somewhat difficult task and it is not clear yet whether the tools for hot-mixes such as the PCG can be used and if so, under what conditions, to estimate the in-place density of cold mixes.

Still, it must be remembered that measuring in-situ densities with cold mixes is not an easy task because the water content is difficult to know with precision. Then, it must be remembered that, even for hot mixes, estimating the in-place density from PCG measurements is not straightforward and needs to first evaluate the equivalent number of rotations corresponding to the planned layer thickness, number of passes and type of roller to be used in the field [MOU 82].

3.1.3. *Mechanical Properties*

Then, the mechanical properties have to be evaluated. In fact, one argument that impedes the development of these technologies at least for new pavements, is the absence of well-known mechanical properties from which pavement structures can be designed. The main difficulty is that the properties are time-dependent due to a time-dependent breaking process and composition, as a consequence of water loss [LEB 00,CAR 02]. This makes it very difficult to just know what would be a representative composition of the in-place mix and from then, what would be a relevant laboratory curing procedure to reach this point. Field results show for example that 1 or 2% of water (based on total mix) invariably remain trapped within the thick cold mix layers which leads to a fluctuation of the water content with time [BRO 02]. The proposal of 14 days at 35°C under 20% relative humidity (RH) seem to be representative of field results after 1-3 years [SER 03], but it can also be argued that this is a somewhat optimistic curing procedure and that depending on the local climate, this final stage might never be attained. In fact, it is documented that 6 months at 18°C and 50% RH was representative of 9-10 months in the field [CAR 02]. Although these curing conditions are more severe than the previous ones, they might still be considered favourable when compared to average European local climates.

Since field conditions vary with location, an optimistic and a pessimistic curing procedures might be necessary to give upper and lower bounds of the possible final properties of the cold mix.

In all cases, it will be necessary to have an estimate of the initial mechanical properties, the final ones but also of the time needed to reach this final stage. This can be done by following any mechanical property versus time, for example compressive strength for thick mixes [LEB 00] or the Dason test or the Benedict cohesion tests for thin mixes [LES 01]. If these properties were to be used for pavement design, it would of course be better to rely on modulus versus time measurements.

But then, what final properties should be measured? Modulus seems to be relevant, but very cohesive materials are not necessarily needed in order to ensure good resistance to traffic induced deformation [BRO 02]. Given the context, the French design manual for pavement structures [SET 97] suggests to use values of 2000 and 3000MPa for the modulus at 15°C 10Hz, depending on the residual binder content (respectively for 3.2 and 4.2 parts per hundred aggregate). Recent measurements confirm this order of magnitude for gravel emulsion [CAR 02].

Fatigue behaviour needs as well to be evaluated in order to design a pavement structure. However, it is well known that the current laboratory procedure can sometimes not be applied to cold mixes simply because their weak cohesion prevents to manufacture test specimens. Moreover, the in-situ fatigue behaviour is known to be excellent [COR 96, LES 02], with a cracking pattern different from

what is observed with hot mixes: First, and very rapidly, a network of micro-cracks appears but which then stabilize and never evolves to the complete network of deep crocodile cracks with subsequent material loss and pot hole formation that is known with hot mixes [LES 02]. Furthermore, even 100,000 wheel passes of very high loads (15t axle load) could not ruin the micro-cracked gravel-emulsions at the LCPC test track, although Benkelman beam deflections of order 140-160 1/10mm were recorded, which corresponded to deformations of order of 500 μ def at the base of the gravel emulsion layers [LES 02].

Therefore, the relevance of the current fatigue testing for cold mixes is highly questionable, especially since the laboratory results would indicate a poor resistance to fatigue [COR 96]. In fact, and given the absence of laboratory values, the French design manual proposes to only design gravel-emulsions based on the vertical stress criterion and not to take into account the fatigue resistance [SET 97].

	Thick layers (Gravel-emulsion, open- or dense-graded cold mix)	Thin layers (microsurfacing)
Water Sensitivity	– immersion/compression with realistic air voids	– abrasion
Workability	– Nynas workability with improved procedure [DEL 02b]	– Diason [LES 01]
Compactibility	– Gyratory Shear Compactor – static compaction	– not necessary (thin layer)
Cohesion Built-Up	– compressive strength – modulus	– Diason [LES 01] – Benedict cohesion test [LES 01]
Final Properties	– compressive strength – modulus – fatigue	– abrasion

Table 2. Potential test methods for the different aspects to be evaluated in cold mix design.

3.1.4. Summary

All these difficulties explain why most of the design procedures still rely on simple procedures such as the compression resistance and water sensitivity as measured by the Duriez procedure [AFN 94b] in France or the

immersion/compression test in Spain [AEN 99b]. Still, the current compaction procedures for these tests yields unrealistic air voids and it would probably be more adequate to change the compaction effort so as to reach a realistic typical air void content, for example 15% for gravel-emulsions [LES 00,BRO 02] or dense graded cold mixes [LAF 85]. From this rapid overview of the current difficulties, we clearly see that formulating a cold mix lacks a well-defined procedure that will address all key points of the final in-place properties of the materials. Still, our knowledge of the way the different formulation parameters interplay help us define a rational procedure in order to optimise mix performance.

3.2. A Rational Mix Design Procedure

A mix design method for cold mixes must, equally to its hot equivalent, lead to targeted final mechanical properties. This can only be done through a tight control of all the components properties and contents. Since we have three components:

- Aggregate
- Bitumen emulsion
- Water

the quality and quantity of each one of them must be defined, together with the amount and nature of possible additives.

Taking into the complex interactions between the components, the design can only proceed via a progressive introduction of each component. Thus, the needed stages for a rational mix design method are as follows [POT 02,POT 02b]:

- Stage 1: Definition of the aggregate gradation
- Stage 2: Definition of a minimum overall water content
- Stage 3: Choice of emulsifier and adjustment of the pH
- Stage 4: Definition of the emulsifier content
- Stage 5: Definition of a minimum emulsion content
- Stage 6: Optimisation of the final composition with respect to the mechanical properties.

Since the general ideas behind this method are summarized in [POT 02,POT 02b], we will not review it in details but focus on the parts than need specific testing that are not currently standardized. The organization of the stages is depicted in Figure 3.

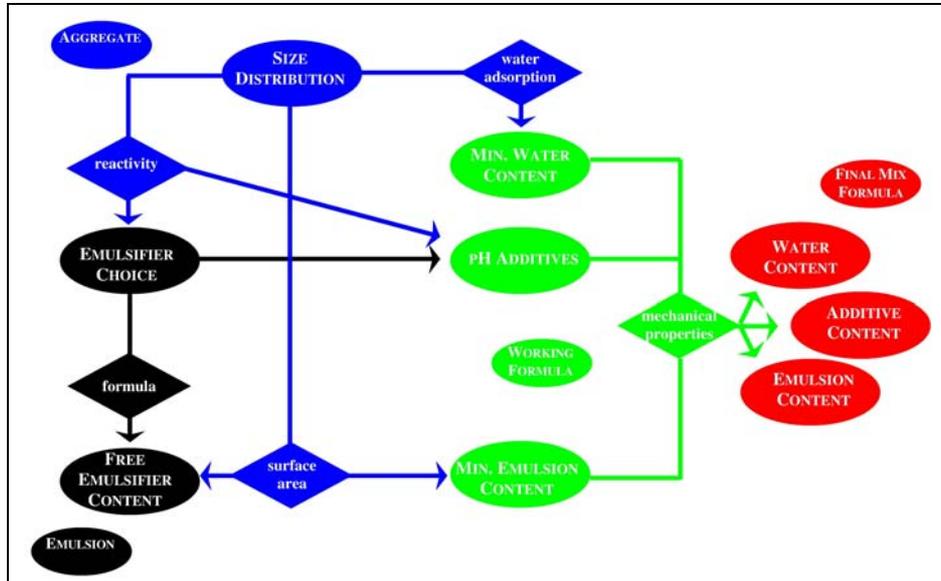


Figure 3. Formulating a cold mix. Each colour corresponds to one system (black: the emulsion, blue: the aggregates, green: the mix working formula and red: the final mix design). The ellipses correspond to the selection of a composition parameter and the diamonds, to a property deriving from the chosen composition.

3.2.1. Stage 1. Definition of aggregate gradation

The grading curve must be defined depending on the intended application (base or surface coarse,...), according to current specifications, and by making sure that the selected proportions allow for a good compactibility. This point is not specific to cold mixtures and since compactibility of cold mixes is difficult to measure in the lab it is better to first rely on existing gradations for hot applications or on experience.

As for aggregate choice, in addition to the traditional standard tests (gradation, sand equivalent and methylene blue value), it is important to characterize the aggregate reactivity and surface area to have a first idea about the possible breaking scenario. This can be done through the pH increase test.

3.2.2. Stage 2. Definition of a minimum overall water content

For the selected granular blend of aggregate size between 0 and D where D is the

maximum aggregate size (hence the notation $0/D$), it is necessary to evaluate the needed quantity of water to insure a good coating. The role of the added water is to prepare the mineral surfaces for coating by the emulsion.

The lower limit corresponds of course to the water content which is naturally adsorbed onto the aggregates and can be directly determined by a Centrifuge Kerosene Equivalent (CKE) test but with water instead of kerosene [ECK 02]. This minimum quantity of water measured by the CKE test is thus interpreted as the minimum quantity required to obtain a good coating.

It should be added that if an excess of water favours the quality of coating, it will however induce a faster cohesion build-up and lower density, and thus lower mechanical properties and risks of post-compaction under traffic. The upper limit depends on the breaking behaviour of the emulsion and will be optimised in stage 6, depending on the required workability characteristics.

3.2.3. Stage 3. Adjustment of the pH

Depending on the aggregate reactivity (which includes its specific area), it is possible to evaluate a theoretical pH of the emulsion-added water-aggregate system. Various means are then possible to counter the strong effect of certain aggregates on the pH, in order to increase the destabilization time (induction time) and its consequences on the breaking, cohesion build-up and quality of coating:

- The choice of emulsifiers (or combinations of emulsifiers) as well as acids allowing to sufficiently delay or to suppress the effects of aggregate reactivity.
- Addition of acid or basic compounds allowing to regulate the pH at mixing stage. This way (insofar as it is possible) is also interesting because it allows one to place himself at optimal values of pH with respect to the surface tension of the bitumen (see Table 1).

3.2.4. Stage 4. Definition of the emulsifier content

In general, so-called “slow-setting” emulsions, according to current technical specifications or commercial names, are emulsions with high residual emulsifier content, which makes it possible in theory to cause a progressive breaking in contact with the aggregates. An alternate method consists in formulating the emulsion so as to have a low residual emulsifier content, and to adjust this value during the manufacture of the bituminous mix by bringing additional emulsifier through the added water.

Whatever the chosen philosophy, the aggregate reactivity and its surface area will guide the formulator in fixing, a priori, a target emulsifier content based on

experience. But the final adjustment will necessarily require some testing (stage 6). Still, the residual emulsifier content is a consequence of the chosen emulsifier/bitumen system, emulsifier content and emulsion particle size distribution. Thus, it is necessary, in order to control the residual emulsifier content, to manufacture emulsions with well-defined and constant particle size distribution. Then, residual emulsifier can be measured [VER 01].

3.2.5. Stage 5. Definition of a minimum emulsion content

A minimum emulsion content can be estimated from the chosen aggregate grading curve (and especially from its surface area), and from the particle size distribution of the emulsion, by hypothesizing that the deposit of a small number of compact mono-layers of bitumen droplets onto the surface of the aggregates is sufficient to obtain a correct coating. Thus, surface area of the aggregates and particle size distribution of the emulsion are sufficient in theory to estimate a minimum binder content, from which it is straightforward to calculate a minimum emulsion content.

Although more work is needed to implement this idea, it is proposed here to refine the concept of the richness modulus [AFN 94], by taking into account the true value of the surface area of the aggregates, and by taking into account the dispersed nature of the binder in the bitumen emulsion.

The higher limit of the emulsion content will in turn be primarily dictated by mechanical considerations (stage 6).

3.2.6. Stage 6. Final composition optimised with respect to the mechanical properties

The preceding stages defined an aggregate gradation, minimum values of the components (overall water, emulsion) and target residual emulsifier content. It is now needed to set the target values for the water content and the residual binder content on the basis of mechanical properties.

The mechanical properties at short times condition the workability. In addition to the climatic aspects which influence the cohesion build-up kinetics, these properties are obviously largely influenced by the amounts and quality of each component, as described above. We propose thus to define the target values of each constituents listed above (total water and residual emulsifier content, adjustment of pH, content in emulsion), of which minimal values were obtained (stages 2-5) thanks to the tests carried out on the aggregates (stage 1), on the basis of mechanical test. This amounts to controlling the contraction kinetics, and the fundamental parameters at hand are listed in Table 1.

For thick mixes, one must then first carry out the Nynas workability test, in order to obtain a cold bituminous mix formula which remains workable during a minimum time of about 2h after manufacturing, depending on the estimated time between manufacturing and laying. Then, PCG tests, when equipped with the water suction device, allow for optimising the bituminous mix toward its in-place density, by primarily playing on the overall water content, also it needs further evaluation as discussed earlier. Of course, a compromise between in-place density and workability will have to be sought for in some cases.

For thin mixes such as microsurfacing, the minimum workability time is much shorter, of order of one minute and is evaluated by specific methods mostly manual but also more advanced ones [LES 01].

Then, tests of accelerated curing can be done on the specimens in order to measure the cohesion built-up and the final mechanical properties. As discussed earlier, the long-term properties of the material might necessitate both an optimistic [SER 03] and a pessimistic curing procedure. Then, the curing kinetics needs also be evaluated and could in principle be maximized for all cold mixes as is done for microsurfacing.

As for the final properties, and as discussed in the former section, we lack experience for the choice of the correct testing to be performed on such materials, and compressive strength, modulus and in some cases fatigue resistance might be measured although the relevance to field behaviour of the latter needs to be better estimated, as a consequence of the peculiar cracking behaviour of such materials [COR 96,LES 02].

4. Conclusions

Recent research allows us to understand quite clearly the phenomenon occurring when a bituminous emulsion is put into contact with mineral matter, as is the case for cold mixes.

This allows us to better control the different stages of the breaking process which eventually leads to the formation of a bitumen film coating the aggregates.

The way it can be used for cold mix formulation is discussed. Still, we show that we lack well defined procedures for the evaluation of most properties that are crucial for the development of cold technologies.

One of the critical aspect that clearly needs more research in order to propose a realistic and consensual testing procedure concerns the prediction of the in-situ density of cold mixes.

Another key aspect which will certainly permit a better development of cold mix technology is a better understanding of their fatigue behaviour and how it should be evaluated in the laboratory. From thereon, designing pavement structures with cold

mixes could be made with confidence using existing methods.

Therefore, the future research shall concentrate on these aspects and try to standardize as much as possible the consensual testing protocols that start to emerge concerning for example workability and accelerated curing.

Without these elements, the development of cold mixes will remain slow because they will keep being perceived as very technical materials, although much is now known of their precise behaviour and the parameters that affect it.

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