CEMENT ADDITIVES
PROFITABLE LIMESTONE CEMENT

REPRINT OF PAPER PUBLISHED IN INTERNATIONAL CEMENT REVIEW AUGUST 2014

BUILDING TRUST

Profitable limestone cement

by Jorg M Schrabback,
Sika Services, Germany/
Switzerland

To increase profitability, producers are seeking to reduce the clinker factor of cement and use other materials such as limestone to produce blended cements. While this presents technical challenges, these can be successfully overcome through the use of high-performance quality improvers.

As cement companies seek to increase profitability, their technology departments look for solutions that enable them to derive profitability from using increasing volumes of clinker replacements. When lowering the clinker factor, limestone offers a very interesting opportunity as its almost unlimited availability compares favourably with other supplementary cementitious material (SCMs).

The cost of limestone raw material (~€4/t) is also considerably lower than Portland cement clinker (~ €25/t) while limestone processing emits far lower CO_2 volumes than clinker. In addition, limestone as a clinker replacement can increase plant output in a fast and economical way, especially in cases where clinker capacity is the limiting factor.

Ensuring cement quality

However, to successfully introduce limestone cement into the market, the plant must keep a close eye on good process parameters to ensure cement quality.

These requirements mean that the following areas issues need to be addressed:

- strength and durability must fulfill the construction industry's requirements
- production rates and process efficiency should meet the targets for low-energy consumption and supplied volumes
- workability of concrete should be on a par with traditional cements.

Strength

The addition of limestone up to around five per cent is generally regarded as constructive due to its positive effect on workability and strength. This is mainly due to improved particle packing effect, the amplification of hydration kinetics due to the nucleation and formation of carboaluminates providing additional space-filling hydrates. [1]

Introducing a higher limestone content into cement often presents challenges in terms of strength, production and workability

Conversely, larger amounts of limestone reduce the strength of standard mortar by 0.5-0.8MPa per additional per cent of reduced clinker factor. With a limestone content of approximately 10 per cent, the positive and negative effects of limestone neutralise each other. Consequently, at 20 per cent limestone content, a 5-8MPa strength loss vs Portland cement has to be considered.

Chemical strength enhancer

Chemical additives offer a fast and cost-efficient solution. So-called strength enhancers or quality improvers (QI), ie SikaGrind-870, chemically activate cement hydration and with this promote the strength development in the range of up to 5MPa early strength and up to 7MPa late strength. [2] The complex process of cement hydration is mainly influenced by dissolution of clinker ions in water, the formation of crystal seeds and finally, the growth of CSH crystals. Chemical strength enhancers influence this dissolution-precipitation process by altering the dissolution rate and the saturation points of specific ions.

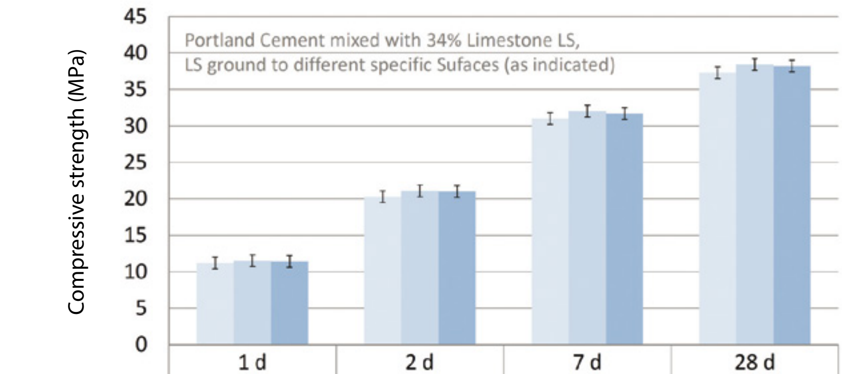
Clinker fineness

The entire process is influenced by particle size. Large particles have a negligible specific surface and hence use only minor parts of their strength potential. Sufficiently-fine particles have a large specific surface and completely hydrate during the hardening time of concrete. In contrast, overground particles with their huge specific surface have no strength potential due to their small volume and extremely fast reaction. The more overground particles are, the higher the water demand of cement. Therefore, the right particle size distribution (PSD) with high amounts of particles in the range 3-30µm is needed. [3]

Limestone fineness

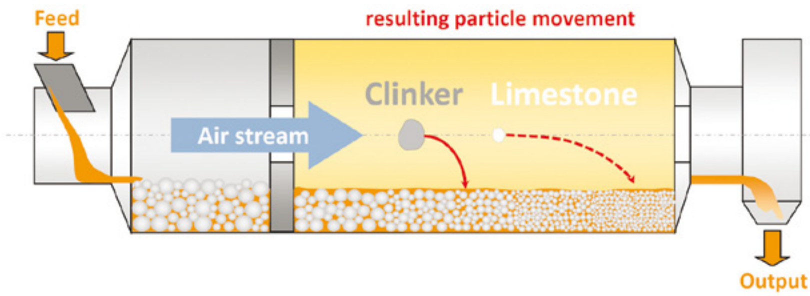
When interground with clinker, resulting limestone particles are, on average, finer than clinker particles (more than 90 per cent smaller than 10µm [1]). Consequently, every per cent of limestone added increases the specific surface in the range of 50-100cm²/g according to Blaine at a constant production rate. In contrast to clinker, the specific surface plays an inferior

Figure 1: effect of limestone fineness on strength



	1 d	2 d	7 d	28 d
LS 4400 cm²/g	11,2	20,3	31,0	37,3
LS 5300 cm²/g	11,5	21,1	32,0	38,4
LS 5900 cm²/g	11,4	21,0	31,7	38,2

Figure 2: mill operation targets for limestone cement production



Targets for mill operation
- Get limestone particles as fast as possible through the mill
- Ensure sufficient grinding of clinker particles

Chemical process additives support these targets
- Improve particle dispersion/reduce agglomeration
- Reduce coating and overgrinding
- Improve production rate, particle size distribution and quality

role in terms of the degree of hydration (DOH) and strength (see Figure 1). Therefore, the higher fineness of limestone cement does not compensate the strength loss from clinker reduction but only adversely affects water demand.

This confirms the findings of the German cement association, VDZ, which state that the fineness of limestone cement measured as specific surface according to Blaine is an insufficient value to predict strength development as well as durability of limestone cement. [4] In plant trials with 30 per cent limestone content and insufficient strength as well as durability, the pure adjustment of the grinding process at similar Blaine values made it possible to achieve more than 50MPa final strength and the lowest scaling in the cube test (frost resistance) which indicates the best durability.

Sika's practical experience shows that the 'secret of success' is to avoid overgrinding limestone particles and ensure sufficient clinker fineness.

Sika's practical experience shows that the 'secret of success' is to avoid overgrinding limestone particles and ensure sufficient clinker fineness.

Ensuring efficiency

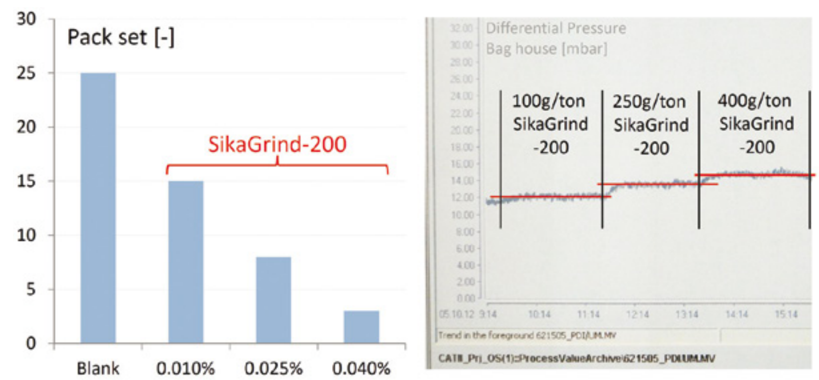
Agglomeration in the mill

Unfortunately, limestone softness and related high fineness present a challenge for mill operation. The finer the particle size, the larger the attraction forces between the fine cement particles (agglomeration) as well as towards the steel surfaces of balls and liners (coating). This increases the amount of overground limestone particles, reduces the grinding efficiency in respect to clinker particles and leads to high water demand and insufficient strength.

Target for mill operation

Consequently, the mill has to be operated with the target to avoid overgrinding. This can be achieved by moving limestone particles as fast as possible through the mill while ensuring sufficient grinding of clinker particles (see Figure 2). One option is to adjust the air ventilation (increased draught) which reduces the mill retention time. Better particle dispersion significantly supports the goal of overgrinding. Chemical process additives, ie grinding aids (GA), neutralise the surface energy of ground particles which in turn reduces agglomeration. Thus, sufficiently-fine and well-dispersed particles leave the mill, making space for the remaining coarse particles (mainly clinker) and hence supporting physical clinker activation.

Figure 3: grinding aid effect on pack-set and bag house DP



Powder flowability

Besides a higher production rate and improved strength development, the dispersing effect can be measured as increased powder flowability using various test methods:

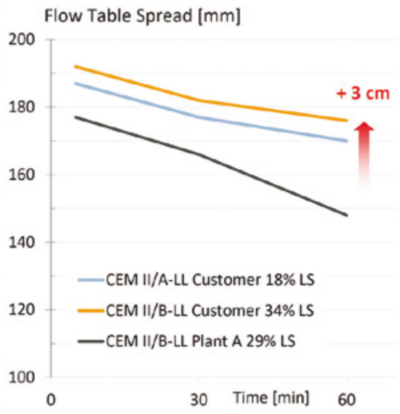
- Bulk density = free-flowing filling of a vessel
- Imse value = sieve passage at defined energy input
- Pack-set = loosening cement cake after previous 'compaction'.

Pack-set is a widespread ASTM C 1565 test method which determines the risk of plugging, bridging or funnelling of cement during storage, transportation and unloading. It is affected by factors such as cement fineness, clinker properties, supplementary cementitious materials (SCM) as well as the type and applied dosage of a grinding aid. Just 250g SikaGrind-200/t of cement is sufficient to achieve the desired pack-set value of a pure Portland cement (see Figure 3).

An additional factor to consider is that stronger-dispersed individual cement particles penetrate deeper into the fabric of bag filters compared to agglomerated cement. This increases the differential pressure (DP) of the baghouse, however, in most cases, it is within the standard range.

Figure 4: case study – limestone cement with highest limestone content using high-performance quality improver

CEM II/B-LL 32.5 R	Benchmark 29% LS	Customer 34% LS
Chemical Additive	300g/ton Grinding Aid	2000g/ton SikaGrind LS-43
Pack-Set [-]	4	2
Water Demand [%]	27.3	25.2
Initial Set [min]	215	170
Final Set [min]	245	235
R_c 2d [Mpa]	20	21,4
R_c 28d [Mpa]	41	42,8



Water demand & workability

The behaviour of fresh concrete – expressed as slump flow or workability – is also a key factor, especially in terms of workability-enhancing concrete admixture costs. High limestone content and increased fineness lead (unavoidably) to higher water demand which generally increases the amount of superplasticiser needed to achieve targeted workability. Cement producers would like to avoid such discussions when introducing new and more environmentally-friendly cements to the concrete market.

Table 1: cement design overview

Raw materials content (%)	Cement formulation			
	1 – Blank	2 – GA	3 – QI	4 – HPQI
Clinker (cost: € 25/t)	85	85	80	75
Limestone (cost: € 4/t)	10	10	15	20
Gypsum (cost: € 8/t)	5	5	5	5
	Cement additive			
	Blank	GA	QI	HPQI
Cement additive dosage (% of cement composition)	0	0.035	0.06	0.15
Blaine (cm^2/g)	4750	4600	4950	5300
Sieve residue (%)	10.2	10.4	7.4	4.4

Table 2: technical performance

Indicator	Cement formulation			
	1 – Blank	2 – GA	3 – QI	4 – HPQI
Strength – early, two-day (MPa)	19.8	21.1	20.7	20.5
– final, 28-day (MPa)	55.4	56.6	55.9	55.5
Production rate (tph)	90	100.8	103.5	106.2
Production rate increase (%)		12	15	18
Cement production at constant clinker consumption & reduced clinker factor (Mt)	1.0	1.0	1.0625	1.1333
Additional cement production at constant clinker consumption & reduced clinker factor (kt)		0.0	62.5	133.3
Specific energy consumption – spend (kWh/t)	41.1	36.7	35.7	34.8
– savings (kWh/t)		4.4	5.4	6.3
CO_2 emissions – spend (t CO_2/t cement)	0.7275	0.7266	0.6849	0.6433
savings in 1Mta plant (kta)		0.9	42.6	84.2

Table 3: economic evaluation

Cost (€/t of cement)	Cement formulation			
	1 – Blank	2 – GA	3 – QI	4 – HPQI
Raw material	22.05	22.05	21.00	19.95
Cement additive (treatment cost)	0.00	0.23	0.93	1.88
Specific energy cost of grinding process	2.47	2.20	2.14	2.09
CO_2 emissions cost	4.37	4.36	4.11	3.86
Total costs	28.89	28.84	28.18	27.78
Total savings (€ /t of cement)	-	0.05	0.71	1.11

This would be possible with a high-performance quality improver (HPQI).

At one European cement plant, the target was to maximise limestone content in a CEM II/B-LL 32.5 R (maximum 35 per cent) while achieving the same workability as CEM II/A-LL 32.5 R (maximum 20 per cent). The external benchmark of an already-supplied cement of the same class, which had a limestone content of 29 per cent with a water demand of 27 per cent, was suffering a significant loss of flow table spread over the first hour. The Application of 0.2 per cent of SikaGrind LS-43 enabled production with 34 per cent limestone, reaching the same production values and workability as CEM II/A-LL 32.5R (18 per cent limestone content) by the same plant and better values in terms of workability and strength compared to the external benchmark (see Figure 4).

This target achievement was the result of a tailor-made cement additive technology, improved mill operation and excellent cooperation between the customer and Sika.

Economic evaluation

While energy is typically the first cost consideration, the resulting cost reduction from a production increase of up to 12 per cent allows for the use of a basic GA to achieve a net saving. This limits the addition of limestone to approximately 10 per cent. Table 1 shows four different cement compositions analysed in terms of technical performance (Table 2) and from an economic perspective (Tables 3 and 4).

Raw material cost

A substantial reduction of around €1m in the annual raw material cost can be achieved by using traditional QIs. These compensate the strength loss of five per cent higher limestone content (eg 15 per cent total limestone content), thereby ensuring net savings of approximately €400,000 when considering energy and raw material costs for a 1Mta cement plant.

Table 4: economic evaluation for 1Mta plant

Cost savings vs blank (€'000/a)	Cement formulation		
	2 – GA	3 – QI	4 – HPQI
Raw materials	0	1050	2100
Additives	-230	-930	-1880
Energy	270	330	380
CO_2	10	260	510
Total	50	710	1110
Additional contribution due to increased sales at reduced clinker factor	0	620	1330
Total benefit	50	1330	2440
Total benefit excl CO_2 saving	40	1070	1930

A higher reduction of raw material costs arising from a 10 per cent increased limestone content can only be achieved with the application of a HPQI in conjunction with process optimisation. This tailor-made product must:

- ensure increased production rates and strength development with good particle dispersion and chemical activation
- compensate the increased water demand due to the high limestone content (eg 20 per cent total limestone content).

Although the significantly-higher treatment cost per tonne of cement compared to QI or GA often deters decision makers, the net savings obtained with HPQI in terms of energy and raw material costs – typically around €600,000 – demonstrate the profitability of HPQI for the plant (see Table 3).

Sales volume

The use of these chemical additives is of special value when a reduced clinker factor is considered. For example, higher cement output can be achieved at a constant clinker production without have to invest in equipment modifications. The additional volume can be handled by the existing grinding systems due to the increased production rate.

This is of particular benefit to plants where production rates are at their maximum due to high market demand and every additional tonne of cement will be consumed. Taking into account the profit of additional sales at the same clinker production rate, net savings rise by around €600,000 for traditional QIs and by around €1.3m for HPQI (see Table 4).

CO_2 emissions

A further benefit is reducing the carbon footprint of cement (see Table 2), providing producers the opportunity to introduce new types of 'green' cement. This will result in CO_2 certificates which are surplus to requirements and hence available to sell. Therefore, net savings rise by €260,000 for traditional QIs and by €500,000 for HPQI (see Table 4). Although the current cost of carbon credits is low in Europe, this could change once a pronounced economic upturn takes place, leading to rising cement demand and the associated increase of cost/t CO_2.

Conclusion

While limestone is an inexpensive and widely-available clinker replacement with and reduces environmental impact of the production process, high limestone content in cement presents technical challenges. However, these can be overcome through the use of chemical cement additives.

The share of limestone that can be incorporated into the cement formulation depends on the selected solution. Blended cements with up to 10 per cent limestone can be produced with a basic grinding aid. Quality improvers that compensate the loss in pure strength enable the production of limestone cement with a limestone content of up to 15 per cent in a cost-efficient way. High-performance quality improvers not only provide the aforementioned benefits of GAs and Qs but also compensate for the loss of workability at very high (eg 20-35 per cent) limestone content. While HPQI lead to much higher treatment costs, they can multiply a 1Mta plant's net savings and easily extend the works' production volume by over 100,000tpa.

The use of chemical cement additives, combined with application know-how, allows cement plants to produce blended cements with limestone as clinker replacement in cost-effective manner.

References

1 BARCELO, L ET AL (2013) 'Portland Limestone Cement Equivalent Strength explained' in: Concrete International, November, p41-47.

2 SCHRABBACK, J M, (2009) 'Finest strength development' in: ICR, September, p75-80.

3 TSIVILIS S, TSIMAS, S, BENETATOU, A and HANIOTAKIS, E, (1990) 'Study on the contribution of the fineness on cement strength' in: ZKG, January, p26-29.

4 VDZ (2012) Chapter V Concrete raw materials and technology, concrete construction technology' in: VDZ Activity Report 2009- 2012, p89.

Figure 5: despite causing significantly higher cement additive costs, QI and HPQI improve the profitability of cement plants

SIKA ADDS VALUE TO YOUR CEMENT

Cement is vital for today's construction industry. The cost optimized production of quality cement which meets customer demands and standards as well as sustainability issues challenges every cement plant individually. Sika offers innovative cement additive concepts combined with a specialized technical support, targeting improved production rates, enhanced strength development and adjusted workability. The reduced utilization of energy and clinker contributes to the profitability of your business.

SIKA SERVICES AG
Tüffenwies 16 · CH-8048 Zürich · Switzerland
Phone: +41 58 436 40 40 · Fax: +41 58 436 41 50 · www.sika.com

BUILDING TRUST

GLOBAL BUT LOCAL PARTNERSHIP

FOR MORE INFORMATION:

WHO WE ARE
Sika AG, Switzerland, is a globally active specialty chemicals company. Sika supplies the building and construction industry as well as manufacturing industries (automotive, bus, truck, rail, solar and wind power plants, façades). Sika is a leader in processing materials used in sealing, bonding, damping, reinforcing and protecting loadbearing structures. Sika's product lines feature highquality concrete admixtures, specialty mortars, sealants and adhesives, damping and reinforcing materials, structural strengthening systems, industrial flooring as well as roofing and waterproofing systems.

SIKA SERVICES AG
TM Concrete
Tüffenwies 16
CH-8048 Zürich
Switzerland

Contact
Phone +41 58 436 40 40
Fax +41 58 436 41 50
www.sika.com

BUILDING TRUST