Depth, the missing dimension in your head

Refiring bricks for a new lease of life

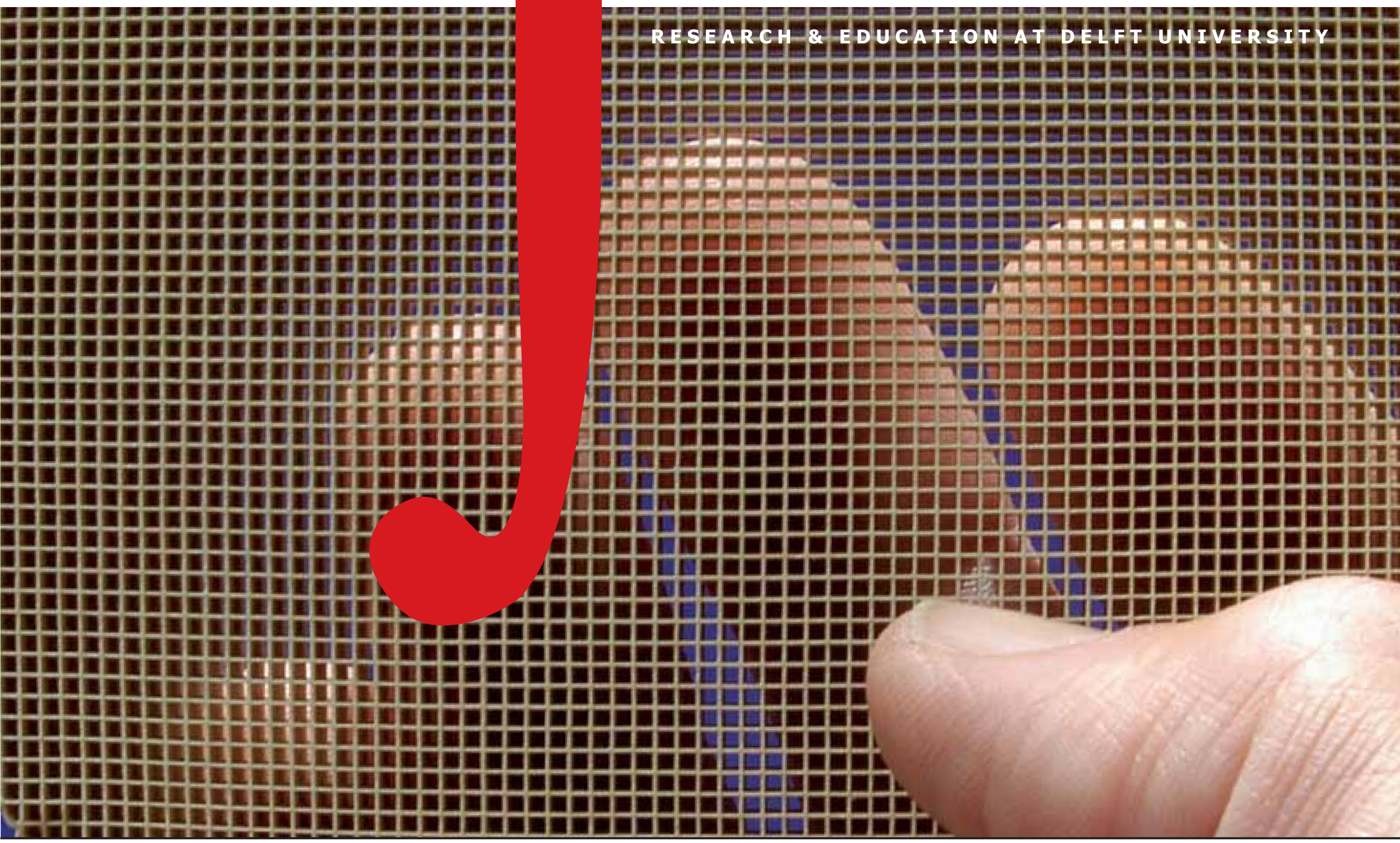
Monolithic reactor: spend less, get more

Steel! Life at the X-ray beam

2004•2

DELFT OUTLOOK

RESEARCH & EDUCATION AT DELFT UNIVERSITY



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COVER: Close-up of monolithic ceramic

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Retaining form in two dimensions

Depth – the missing dimension – is inside the human head

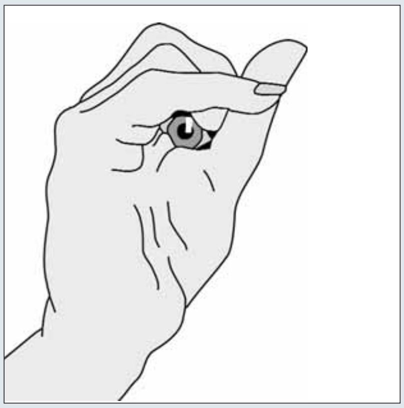
by JOOST VAN KASTEREN

It happens all the time. Seduced by a glossy catalogue or an image on a web site you step into the shop to buy yourself a new toaster or computer display. Once there, disappointment strikes. The toaster is just another tin box, and the sleek computer screen from the brochure turns out to be huge.

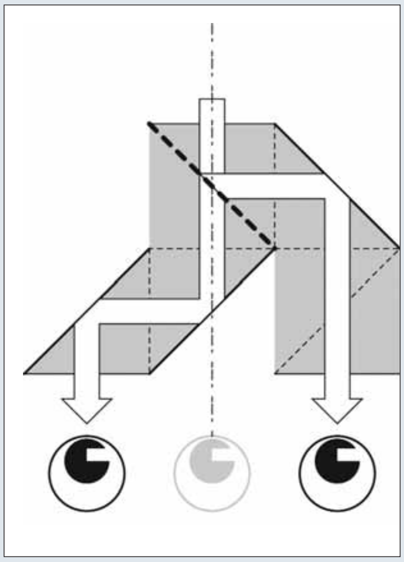
The reverse also happens. For example, a statue in a museum can look much better than it did in the catalogue. All in all, it is quite difficult to retain three-dimensional proportions in two dimensions. Dr. Ans Koenderink of the Faculty of Industrial Design at TU Delft, together with her doctorate student, psychologist Els Cornelis, can quantify the percept of three-dimensional forms in images by using a suitable psychophysical measuring method.
When objects or situations are represented in a photograph, we must fill in the third dimension for ourselves.
'In fact, a photograph of say, a statue or an electric iron is just an array of spots on a piece of paper. It isn't until you actually look into the picture that you discover the statue, or whatever it shows. As you look at the image, you create your own 'pictorial space' in three dimensions. Actually, there is no such space, it is simply a concept inside our own head,' says Ans Koenderink, who is a physicist and associate professor at the HICD (Human Interface Communication Design) section of the Industrial Design Faculty. The other part of the week she works with her husband, Jan Koenderink, at the University of Utrecht where he holds the chair of 'Physics of Man'.
The concept of pictorial space is one we are all familiar with. We do not know if this is an innate faculty, but we do know that children from about the age of three onwards can see 'depth' in pictures. As the cave drawings at Lascaux indicate, pictures were more than a simple pattern of spots to prehistoric man too, even though it wasn't until the fifteenth century that painters learnt to use vanishing points to create true perspective in their work. In all probability, animals are incapable of extracting depth information from flat images, with

Using a synopter, a special type of binocular viewer, both eyes are presented with exactly the same image. If the device is used to look at a flat image, the depth range increases dramatically. The difference between normal vision and looking through the synopter can be as much as 4 times.

^ Ideal City by Piero della Francesca (1420?-1492). This renaissance artist used linear perspective that produces a strong impression of depth in the flat image.



Painters, photographers, film makers, and designers all know that a scene can be flattened by framing it or looking at it through a hole.



The light paths inside the synopter.

The synopter built by Ans Koenderink.

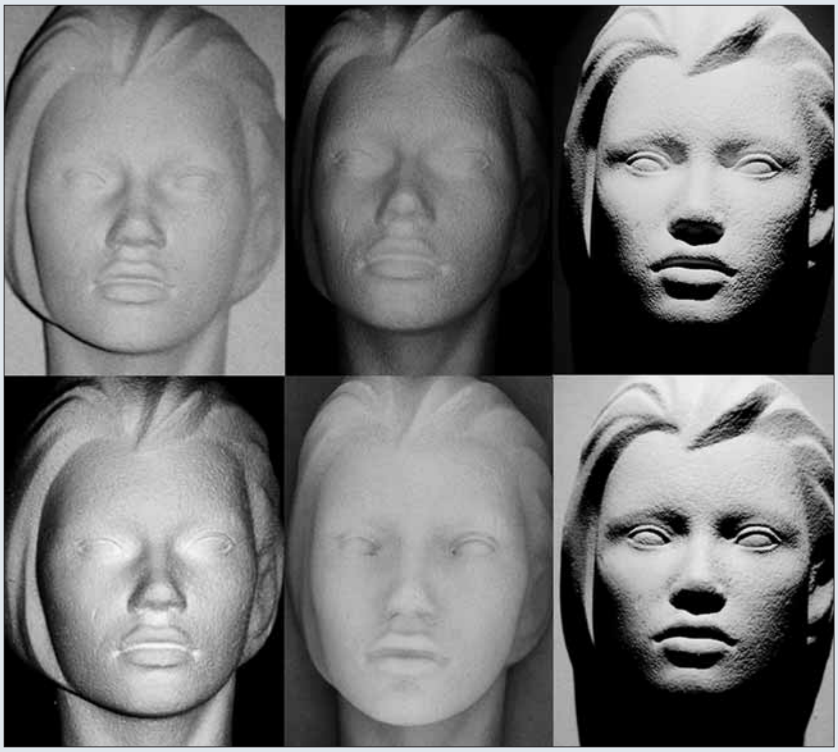
The synopter in use.

the possible exception of the chimpanzee. A cat apparently watching television sees moving patches of colour, but nothing resembling a person or an object. Pictorial space is not the same as perception. The latter has more to do with the way people discern things, i.e. set them off against their own experiences and expectations. The pictorial space is something between physics and psyche. It consists of the visual field (the two-dimensional image created on the retina) and the perceived depth created by our brain. Rather than a true three-dimensional space, it is a '2 plus 1' space, in which the '1' stands for the mentally-added depth. In this context, the German sculptor, Hildebrandt, who lived in the nineteenth century, likened depth to a stream that flows away from or towards one.

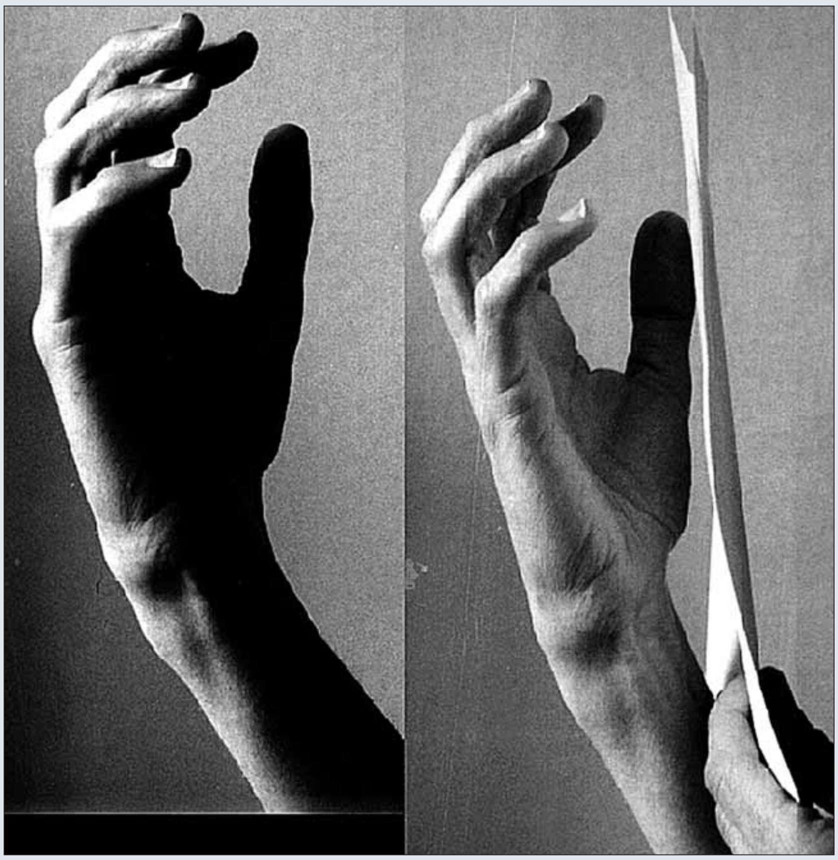
Shop dummies ¶ Over the past years, Koenderink and her husband have developed a number of ingenious methods to measure the imaginary third dimension in order to quantify the pictorial space.
'We will set up a scene in three dimensions,' she explains, 'mostly using shop dummies. We then take several series of pictures, varying such things as the position and pose of the dummies, the lighting, and the texture, all of which can act as cues to help us see depth and the way we perceive an object. The photographs are then shown to test subjects who fill in the third dimension.'
Filling in the third dimension can be done in a number of different ways. In each of them, the test subjects are placed in front of a computer display, with their chins resting on a support to fix the distance from the screen. The subject is then presented with an image and asked for instance to move an arrow on the screen to indicate the direction of the gradient (that is, the direction of steepest rise or fall) of the relief. In another method, the test subject is asked to reshape a straight line crossing the image so that it follows the perceived depth pattern of the shop dummy along the line direction.

Drawing pins ¶ A third measuring method uses a kind of virtual drawing pins (specialists in this field call them thumb tacks). The test subject is asked to adjust a marker in the shape of a circle with a needle protruding at right angles to it (like an inverted drawing pin) until it fits the image. The attraction of this method lies in the fact that the drawing pin markers form part of the mental pictorial space, as it were, whereas the elements used in the other methods – arrows, bars – are projected onto the dummy and therefore form part of the physical space.
Because the drawing pin marker is within the pictorial space, adjusting it requires little effort. Most of the test subjects find it a natural process and manage to automatically adjust each marker in what they consider the right attitude within one second. There are a few people who do not manage to adjust the markers on an impulse, and who have to think before they can act. Koenderink: 'If the group includes such persons – although slim, the chances aren't nil – they will be excluded.'
Suitable subjects are asked to adjust several hundreds of markers in each image. The slant and tilt of the gradient under the marker can be calculated from the attitude of the needle and the distortion of the circle (which becomes an ellipse). The locations at which the markers are to be adjusted, although given in random order by the computer program, are certainly not randomly selected. They form the vertices of a grid of identical and equilateral triangles stretched over the dummy and invisible to the test subject.
Koenderink: 'In fact, it is simply the old-fashioned triangulation method surveyors have been using for centuries to measure distances. As we can calculate the slant and tilt of each triangle, we can use the distortion of the triangles to produce a relief map, the pictorial relief observed by humans. Although, unlike the physical space with three equivalent spatial directions, the pictorial space is non-Euclidian, we can still use this method to measure the depth people see in a photograph or a painting.'

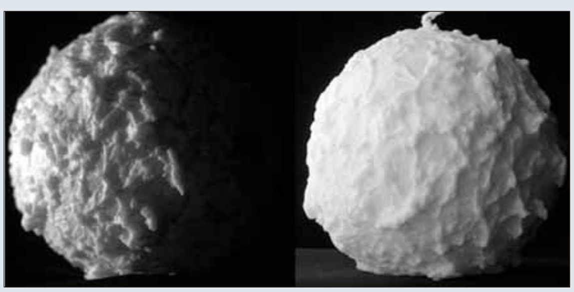
Room for variation ¶ Once you can measure the mental depth, you can also find out how it is affected by cues for seeing depth, e.g. distance. The more distant an object appears in the pictorial space, the flatter the relief observed by people. Or take lighting. With the light shining on the object from the front upper lefthand corner, anything protruding will be pulled to the front upper left. The light source appears to suck in details.
Koenderink: 'All of these effects have been known for some time. Artists have been using them for centuries. The great thing about our measuring method is



Another example of the effect the type of light has, this time also varying its direction. The same mask was used in each of the pictures, but in the upper row it was painted white, whereas in the lower row it was grey. All these variations affect the form percept.



An example of yet another way context affects form perception is the reflection of light. Two pictures of the same hand, with the one on the left being lit from one side, while the one on the right uses added reflective lighting from a sheet of white paper.



The way in which we observe a certain object is greatly affected by the type of lighting. These images show different photographs of the same candle. The one on the left was in collimated light, and the one on the right in diffuse light.

that it enables you to determine how strongly the light source attracts things. There can be as much as fifty percent difference in this.'

In addition to photographic cues, another matter that affects the perception of depth is the task the test subject is asked to perform. This may appear inconsistent, but as Koenderink explains: 'You have to realise that there are in fact an infinite number of ways to fill in the third dimension when you look at a picture. Although the cues in the picture restrict your freedom to interpret to some degree, it still leaves enough room for variation; relatively speaking that is. It is not as if you will suddenly see something completely different.'

Car ¶ As mentioned, artists and designers make full use of techniques to influence the observer's experience of depth by means of all sorts of tricks such as shading, distance, and vanishing points. The quantitative measuring method developed by Koenderink and her husband allows for a much more structured approach, and introduces ways of adapting the object itself to create the required depth effect. As an example she takes a new car design generated by computer. If the design were to be taken into production straight from the digital drawing board, the result might well be far from pleasing, as the increase in scale would cause all convex and concave surfaces to be visually flattened. To prevent this from happening, car designers still have to make a full-scale clay mock-up. The measuring methods devised by Koenderink and her husband could put an end to this. Other objects too, whether real or virtual, could be rendered in a more realistic perspective, for instance a design for a new chemical plant.

Koenderink: 'It's early days yet as far as understanding pictorial space is concerned, in other words the way in which we see depth and how it is affected by the different cues and the way they interact. What we do have now is a kind of yardstick to measure the pictorial space, which enables us to gather empirical data and test our assumptions about the way we see things. This will prove to be a very useful tool for designers.' n

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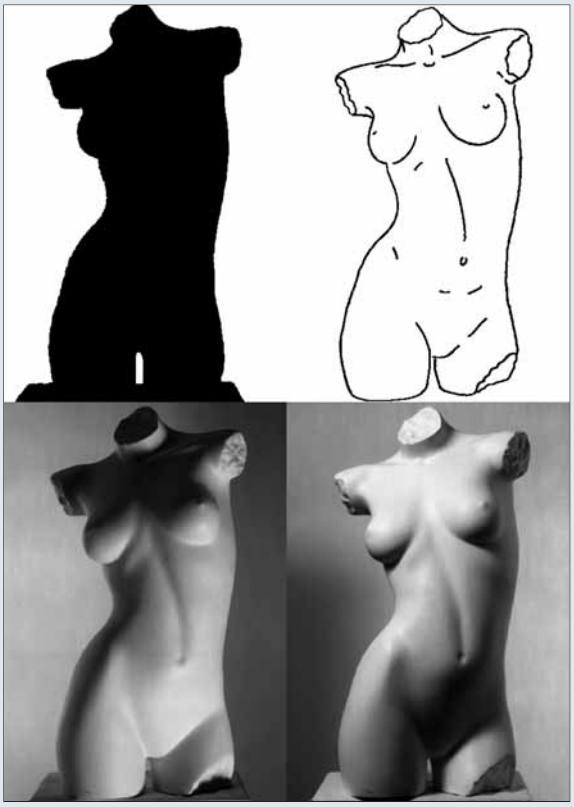
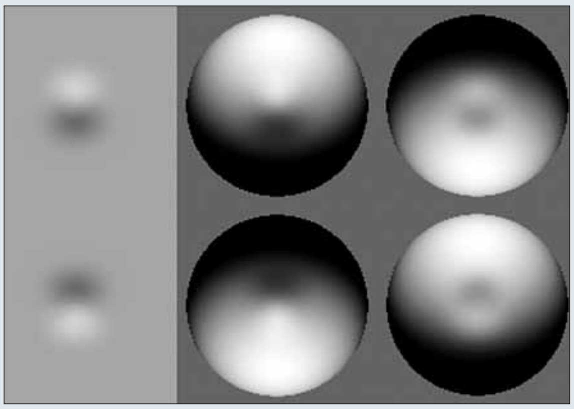


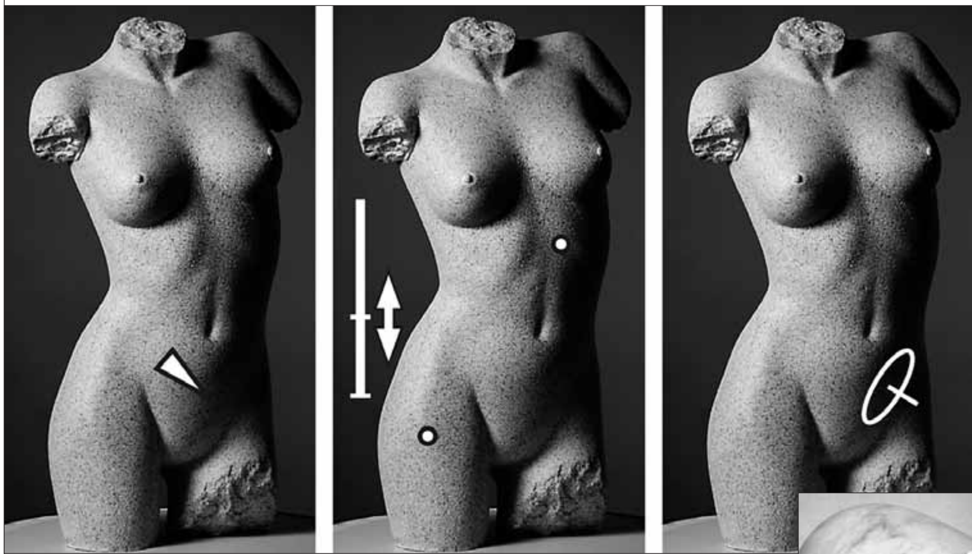
The lower row shows another example of the effect the direction of the light source has. The upper row on the other hand gives an example of the way the method of depiction (silhouette versus cartoon drawing) affects the form percept.



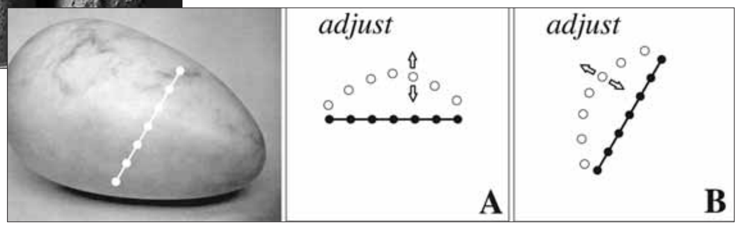
The effect of context on the perception of form. We have three situations, in each of which two light/dark shapes ('pimples') are shown. Depending on the context, these light/dark shapes are interpreted in different ways in their depth percept.

Part of the studio in which the stimuli for the experiments are photographed.

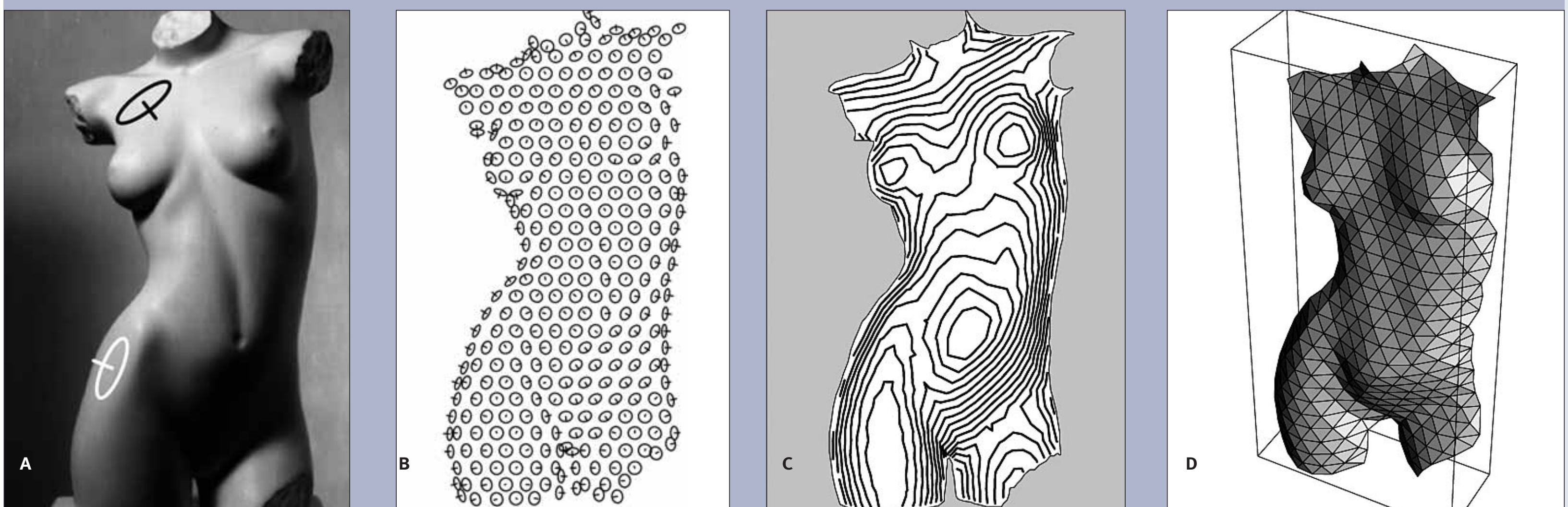
Some simple shapes Koenderink uses to demonstrate the interaction between the light field and the perceived shape.



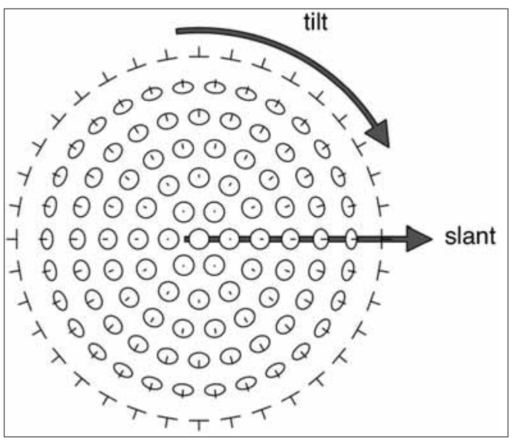
Dr. Koenderink uses a number of different measuring methods to quantify the form percept. The leftmost image illustrates the adjustment method, in which the test subject adjusts a gauge graphic, such as an arrow or a line, to a certain property of the form to be measured (e.g. the direction of a gradient). The image in the centre is an example of a reproduction task, in which markers outside the object have to be adjusted to indicate properties of the object. On the right is the fit method, in which the test subject is asked to merge the gauge graphic (which in this case is shaped like a drawing pin) with the form.



In this adjustment method, the test subject is asked to use a computer mouse to distort a straight line drawn across the form to match the depth pattern of the form along this line.

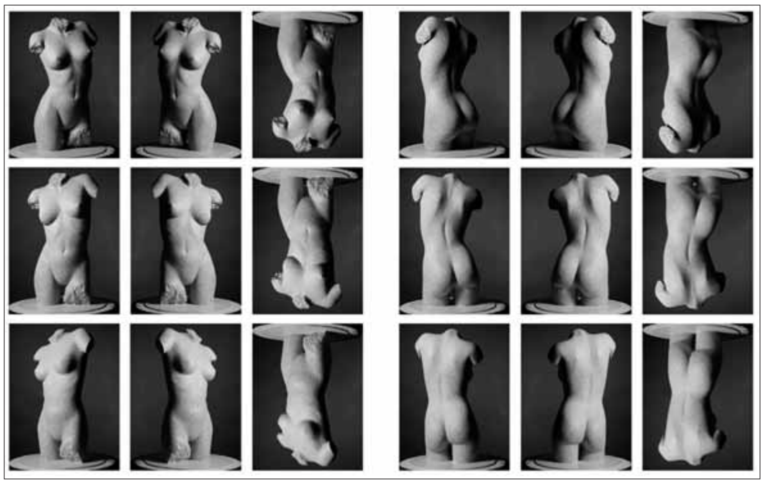


The experiments described in the article use the fit method with the drawing pin marker. The test subject is asked to adjust a circle with a line projected from it at right angles (like a drawing pin) until it fits the form of the depicted object. In the example the marker on the leg is correct, whereas the one on the shoulder is wrong (A). The computer generates the different locations to be marked by the test subject in random order. The locations are determined by triangulating the object (a process that remains invisible to the test subject). Figure B shows the result of a measurement. The measurements are used to calculate the 3D reconstruction. This is visualised by an image (C) showing contours (lines that connect points of equal depth) and a relief image (D).



This figure illustrates the concepts of slant and tilt. This figure shows how slant (the steepness of the gradient) has been plotted in the radial direction, with the tilt (the direction of the gradient) being plotted in the angular direction.

This figure illustrates tilt using a compass course (τ) and slant (σ) as the angle between the direction of view and the outward direction perpendicular to the surface.



The complete set of stimuli as used in this experiment devised by Els Cornelis.

View showing a subject (in this case, doctorate student Els Cornelis) using the test set-up. To ensure a constant viewing distance, a chin rest is used. The eye patch is to ensure that the test subject uses only one eye to view the scene. The markers are adjusted using a computer mouse.

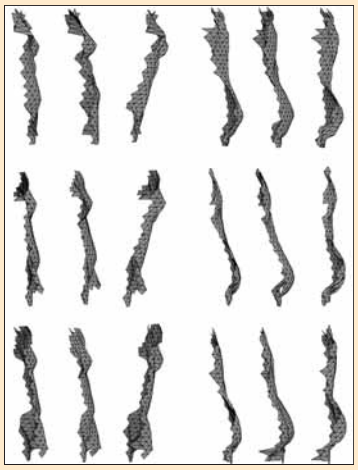
Mirroring

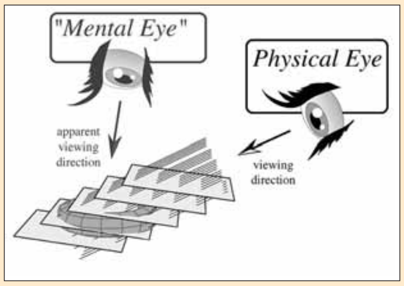
Normally when looking at an object, people will move their head, or walk around it to get a feel of the dimensions of the object. If the object is represented by an image, the image can be moved about, but you cannot see what is behind it, since the observation point has been fixed by the camera.

Els Cornelis, who graduated in experimental psychology at the Catholic University of Louvain, is doing doctorate research in the field of visual perception at the Faculty of Industrial Design at TU Delft. One of the things she looked at is the extent to which our perception of depth, say our pictorial space, is affected by mirroring an image around its Y-axis (left to right) and X-axis (top to bottom). She asked test subjects to use the drawing-pin depth-measuring method outlined in the article on pictures of a shop dummy that had been mirrored along the Y-axis and X-axis, together with the original, non-mirrored images. The up-down mirrored pictures in particular resulted in considerable flattening and tilting of the object in pictorial space.

Analysis of the data showed that the transformation for the most part resulted from the fact that the test subjects had shifted their *mental* point of view. They were in fact trying to see over or past the image. Since the position of their head had been fixed by the chin rest, this means that they had shifted their mental point of view, causing the pictorial space to be affinely transformed, i.e. flattened and tilted. Koenderink had detected a similar phenomenon earlier, when the test subjects were asked to distort a straight line to make it follow the dummy's relief pattern along this line. In that case too, the perceived depth changed when the direction of the line was changed.

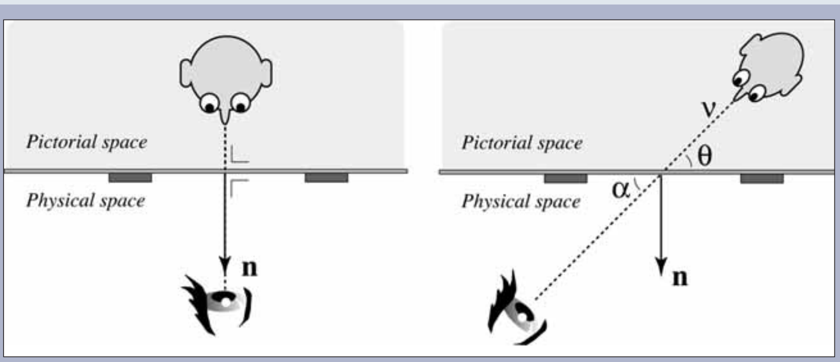
Koenderink: 'However, when you analyse the resulting data, you find that the subjects shifted their mental point of view, and that the change can be as much as sixty degrees.'





Visualisation of the mental viewing point shift.

◂ An example of the results of the experiment. This clearly shows the tilting effect on up-down mirrored images.



A special case of viewing point shift is the eerie phenomenon in which the eyes of a person in a picture appear to follow you around the room. According to Koenderink this is to do with the picture frame, which exists in the physical space, the optical space (the image entering the eye), and in the mental pictorial space, and as such acts as a wormhole between the different spaces. An experiment was set up to measure the pictorial relief of an object in a picture frame when viewed from the front and at a 45° angle. The resulting reliefs did not differ significantly, in other words, the pictorial space is similar. Whatever the viewing angle, you are always looking in the same image direction, which is why the eyes appear to follow you around the room.

Hot masonry and magnetic separation close the brick recycling process

Refiring bricks at 540°C

The Netherlands produces approximately 16 million tonnes of stony building and demolition waste each year. Most if this comes from buildings erected during the nineteen-thirties, sixties, and seventies. Buildings from the nineteen-sixties are characterised by their high concrete content, whereas during the nineteen-thirties masonry was almost exclusively used.

by ASTRID VAN DER GRAAF

For many decades, stony debris from building and demolition sites was reused as road building material. Until recently there was no need to look for other uses for this mixture of concrete and masonry rubble. However, now that our supplies of marl and gravel (two of the three ingredients of mortar and concrete) are dwindling and prices are beginning to rise, the concrete industry is showing a growing interest in ways to recycle concrete rubble. Since masonry rubble can only be used as a granulate for road construction in combination with concrete rubble, a vision of a masonry rubble heap without any takers looms ahead if no alternative application is found. Anticipating the problem, civil engineer Koen Van Dijk of the Civil Engineering Materials Science department at TU Delft has developed a number of processing techniques for reusing masonry rubble. Van Dijk was recently gained his doctorate for developing a process that can extract 50% of the bricks from masonry debris from buildings that have been dismantled selectively. He also uses a magnetic technique to extract the brick fraction from the remaining masonry debris. Mixed with fresh clay it becomes the raw material for a new generation of bricks, thus closing the clay brick cycle.

Each year 23 million tons of construction and demolition waste are produced in the Netherlands. The stony fraction of the rubble is about 70% . The Building Materials Decree stipulates that as of the year 2000 reusable waste may no longer be dumped as landfill. Since it may not even be transported across provincial boundaries, municipal authorities were left with few options apart

The large stream of demolition waste has made the recycling industry into a flourishing trade with a modern approach. Whereas previously the waste would be removed in mixed form to be sorted elsewhere, these days mobile waste separator plants are moved in to extract useful end products on site.

from the obvious one, which was to use all of it for road construction projects. The volume of construction and demolition waste is sufficient to construct a six-lane motorway 340 kilometres long, i.e. the length of the Netherlands, every year. However, now that the government has decided not to build any more roads to tackle the congestion problems, the demand for road construction granulate will inevitably drop. On the other hand, the supply will not, according to Dr. ir. Koen Van Dijk.

Delft Ladder ¶ In anticipation of this development, the TU Delft and TNO Environment, Energy & Process Innovation, based at Apeldoorn, started a research programme to investigate the possibilities for high-quality, sustainable reuse of stony debris.
Although road construction granulate is a useful application, it remains a low-quality form of reuse from the point of view of sustainability. Recycling involves reusing the waste material for the same purpose as it originally served, in this case by having the waste material continue as construction material in its own cycle. This is the only way to close the cycle.
In doing so Van Dijk is introducing the 'Delft Ladder', the modern-day successor to Lansink's Ladder, which dates from 1979, when legislation to control the use of waste materials was introduced. In this context, the use of concrete rubble for the production of concrete is a high-quality form of reuse. Van Dijk's supervisor, Prof. Dr. Ir. Charles Hendriks of the Civil Engineering Materials Science department, is one of the people behind the current Building Materials Decree and the Delft Ladder.

Concrete ¶ The stony rubble produced by demolition activities generally contains about 65% concrete rubble and 35% masonry debris. According to Van Dijk, reuse of crushed concrete rubble is now a viable option, although there is still room for improvement. Broken and crushed concrete rubble produces a jagged granulate in which the particles do not move smoothly against each other.
Van Dijk: "Concrete must be fluid. We measure its consistency by pouring the concrete mix into a conical cylinder, which is then removed. The extent to which the concrete then settles, tells us something about its consistency. Each application demands its own degree of liquidity. For example, a floor requires a higher consistency than a column or a beam."
By adding a superplastifier, a kind of lubricant, the consistency can be increased while maintaining the water/cement ratio. Van Dijk's colleague, doctorate student Hiroshi Ishiguro, is looking further into this part of the stream. The main problem when processing concrete debris is the remaining mountain of masonry debris, which is unsuitable for use as road construction granulate due to its low compression strength and high water absorption rate.

The weakest link ¶ The bond between bricks and mortar is the weakest link, one that has presented many a (DIY) bricklayer with all sorts of problems. If the brick is to dry, it extracts too much water from the mortar. As a result, the cement at the brick face receives too little water when it sets (hydration), and produces a weak bond. If, on the other hand, the brick is too wet, the mortar in contact with the brick receives an excess of water, resulting in cavities as the water evaporates. In fact, it is practically impossible to get it just right, according to Van Dijk, so the lesser of the evils is the thing to go for. As he was supervising a first-year lab session, Van Dijk got the idea of heating lumps of masonry.
"The students had been asked to measure the linear expansion coefficient of an aluminium beam, which is a standard lab assignment. And then I suddenly got the idea, if all materials have different expansion coefficients, why shouldn't bricks and mortar? And if the difference is big enough, the resulting stresses will break the bond."

Burnt shells ¶ "Under laboratory conditions, the masonry spontaneously fell apart after being heated to a temperature of 540 °C in a gas kiln. This temperature raises the stresses to a maximum, and you can hear the mortar bricks bond break loose. Afterwards, you can simply pick the mortar off the bricks in slabs, leaving the bricks almost perfectly clean. The only blemishes are where the mortar water has seeped into the brick, leaving a grey bloom.
The trick only works with cement-based mortar, which is a hard material, creating stresses between the bricks and the mortar.
"The old-fashioned lime mortar, which is made from burnt shells and sand, is

One of the most important end products is mixed granulate. This consists of at least 60% concrete granules and up to 40% mixed bricks and mortar fraction. It is used as a foundation material for road construction. However, the number of road construction projects is decreasing, and with it the market for the recycling industry.

The concrete industry is not an alternative market for the mixed granulate, due to the high content of bricks and mortar. The industry is interested in the pure concrete fraction however, but this still leaves the brick fraction to be disposed of.

The demolition industry is also looking for alternatives, one of which is selective demolition. During the demolition of a simple structure at the Boezembocht marshalling yard in Rotterdam, various waste streams were extracted separately during the actual demolition process.

With a view to reuse, large chunks of masonry were extracted in one piece and sent to the brick-works. The remaining fractions to be extracted were concrete rubble, mixed stony rubble, metal, steel beams, roofing materials, wood in a number of graded qualities, and a mixed residual fraction.

much softer and follows the expansion of the bricks. Anyway, lime mortar is easily removed by hand, which is how bricks reclaimed for restoration projects are processed. These days however, 80% of all masonry uses (Portland) cement mortar, which cannot be removed by hand.”

Experiment ¶ Van Dijk put his theory to the test in Rotterdam, where an old building on the ‘Boezembocht’ railway marshalling yard was being demolished. Van Dijk had arranged for the masonry to be selectively demolished. Timber, metal, and plastic materials are always selectively stripped, but the concrete and masonry shell usually gets crushed to bits and carried off as debris. For his field experiment, Van Dijk needed a couple of tons of ‘unbroken’ parts of wall that could be stacked on top of lorries and carted into the gas kiln. This meant that the demolition plant had to remove the outer leaf of a cavity wall as a separate piece, which can be tricky if both leaves are connected with anchors. For his thermal treatment of the lumps of masonry, Van Dijk got the support of one of the largest manufacturers of bricks and roof tiles in the Netherlands, Terca Brick in Reuver, Limburg, whose technical manager, Ing. Fons Wagener was a member of Van Dijk’s supervisory committee. Using a thermal treatment procedure involving 3 hours of heating up, 2 hours at 540 °C, and then the cooling stage, he managed to reclaim 45% of the bricks from the masonry in one part. Not a bad result for the first field test.

Firing bricks

Fresh bricks are fired for 40–60 hours at a temperature between 1,000 and 1200 °C, depending on the type of clay used. The unfired bricks are stacked on kiln lorries that run on tracks through a 120-metre long tunnel kiln. At the first stage, the dried clay bricks are slowly heated to remove any free, physically or chemically bound water. Up to 100 °C the free water, i.e. the water between the clay granules, evaporates. Between 100 °C and 250 °C the physically and chemically bound water disappears. As a result, the brick shrinks by a few percent. Any organic material left in the clay burns off as the temperature is increased to 250 or 500 °C. Heating to full temperature takes about 20 hours in all, the same time as the cooling down stage takes, although it varies according to the type of clay used. Next to the evaporation of water, the so-called quartz phase transition that occurs during heating and cooling is a major factor affecting the success of the firing process. The transition occurs at 573 °C, when alpha quartz transforms into beta quartz, abruptly expanding its molecular structure. During the heating phase, there is less risk of cracking than there is during cooling since the compression stresses resulting from the transition are easier to absorb while the particles are still relatively loose. During cooling, the tension caused by the shrinkage associated with the quartz phase transition will more easily cause damage. During the actual firing stage, or solid-phase sintering, molecular bonds are formed between the clay particles.
Dr.ir. Koen Van Dijk: “It is a bit like leaving a bag of sweets in a car on a hot day. At the points of contact, the sweets will stick together, and if you try to take one out of the bag, you’ll find the whole lot clinging together.”
To ensure proper adhesion between the particles, a lutum content of 10% is required. Lutum is the fraction of particles with diameters of 10 micrometres or less. The smaller the particles, the better the green strength before firing, and the higher the quality of the brick. However, at higher lutum levels, the risk of cracking due to shrinkage during drying increases.

Subtle demolition ¶ The thermal method for reclaiming bricks is advantageous from an energy point of view. Also, it requires less energy than is required to fire new bricks (see separate box). The drawback is that the breakers, the recycling companies, have to ensure that parts of walls are retrieved in one piece from a demolition site. After all, subtle demolition is a contradiction in terms. Before the process can be applied in the real world, research will have to be done into developing a new approach to demolishing buildings, according to Dr. Peter Rem of the Raw Materials Technology section at the faculty of Applied Earth Sciences. Rem specialises in the deployment of tested and tried separation techniques from the mining industry for new applications. He thinks it is not such a bad idea to heat a building in its entirety.

To recycle the masonry rubble, a thermal process was developed by TU Delft in collaboration with TNO to extract the bricks from the masonry rubble. The masonry was subjected to a heat treatment in the chamber kilns of the Terca window lintel factory at Reuver, Limburg, in the south of the Netherlands.

In three hours, the rubble was heated to a temperature of 540 °C. After two hours at that temperature, the cooling stage followed. The bricks, which had been stacked high inside the kiln, had broken apart from the mortar and tumbled from the kiln lorry.

The cracks at the brick/mortar interface are the result of the difference in linear expansion coefficient.

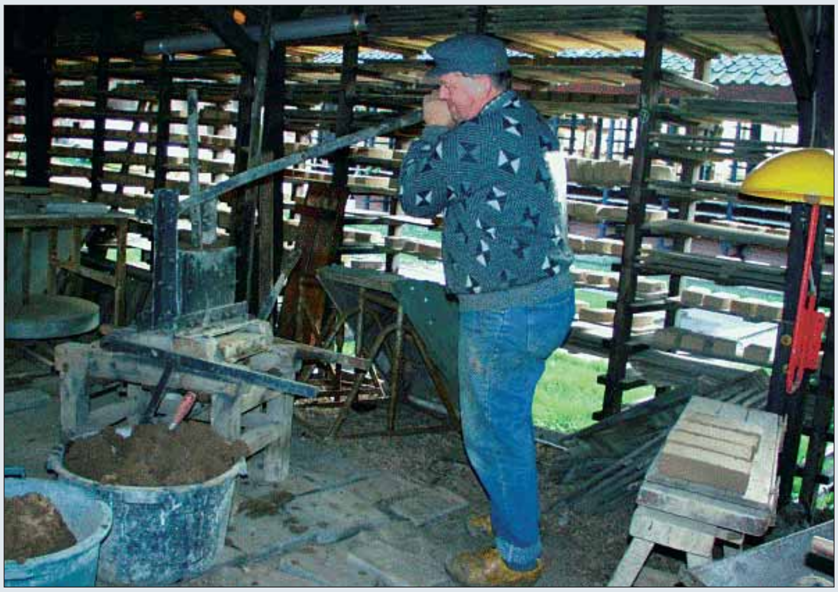
By reclaiming the retro bricks, the recycling loop has been successfully closed. It is now up to the industry to apply the method in the field.

"It may sound strange, but from a logistics point of view it makes sense. If the integral heating of a building becomes part of the demolition process, it stands a good chance of success. The process is simple: wrap up the building and turn up the heat."

Magnetic bricks ¶ Even so, a large part of the masonry remains as rubble. While searching for a suitable method to separate the remaining bricks and mortar from each other, Van Dijk came into contact with Rem. The ideal separation technique was easily decided when it turned out that clay contains about 5% iron.
Rem: "Magnetic separation is used in the mining industry to extract ilmenite ($FeTiO_3$ – ed., AvdG). To separate bricks and mortar properly, the rubble must be crushed into particles with a diameter of no more than 2 millimetres, otherwise the magnet will not be able to handle them. You need a steep magnetic gradient, and as a result the useful field is very narrow. Surprisingly, all bricks are magnetic, even the yellow ones, which you would expect to contain less iron, as their lime content is much higher."
An iron content of 2-3% turns out to be sufficient to separate masonry rubble into brick granulate and mortar grit.
Van Dijk: "If the difference in magnetic susceptibility is big enough, materials can be separated using a magnetic field. The average magnetic susceptibility of bricks is 550.10^{-9} m^3/kg, and that of cement mortar is 17.10^{-9} m^3/kg. This enabled us to achieve an efficiency of 90% for separating bricks from cement mortar."
What remains now is a large container of pure brick granulate of 2 mm or less in diameter. Van Dijk used this to fire his own bricks, with the support of the ceramics department of TNO-TPD at Eindhoven, and Terca Brick. In order to find the ideal mixture of clay and brick granulate, Van Dijk tested a number of variations of clay types, quantities, and types of granulate.
"In the lab, we were still able to obtain good-quality bricks using 95% brick granulate and 5% new clay. These met the various product specifications such as compression and tensile strength, resistance to frost damage, and water absorption. In practical conditions, however, 50% recycled material turned out to be the limit.
"This has to do with the 'green strength', which is the strength of the dried clay brick," Van Dijk explains.

Green strength ¶ The natural colour of clay is greenish. After the fresh clay, or in our case, the granulate mix, has been formed by pressing it into a brick mould and releasing it, the wet brick must dry before it can go into the kiln. The dried, 'green brick', must have a tensile strength of at least 0.5 N/mm^2, because it needs to withstand the internal transport through the brickworks and also to survive the stacking inside the kiln. Speaking of colours, the red colour of the brick we all know so well is produced by the firing process inside the kiln. There are two different ways of firing bricks: oxidising, which means that extra oxygen is added to the kiln, and reducing, which takes place in a closed environment with a shortage [***depleted***???***] of oxygen. During an oxidising firing, the iron in the clay reacts with the added oxygen to form iron oxide (FeO), which has a red colour. During a reducing firing, the bricks end up blackish due to the elementary iron (Fe). If the bricks contain a lot of lime, the resulting calcium oxide (CaO) turns them yellow, and the presence of certain metals such as manganese and copper, lends them a greenish or blueish colour. Van Dijk was surprised to discover that even with a level of yellow brick granulate as high as 75%, the fresh clay type determined the end colour of the brick.
"A cross section of the brick shows the yellow particles"

Infrastructure ¶ This closes the cycle, according to Van Dijk, but the path to actual application is arduous, depending as it does on several different parties in the market. The separate reuse of concrete and masonry rubble affects the entire chain, from demolishers, crushers, recycling companies and manufacturers of building materials, right up to builders and architects.
"The linchpin is formed by the recycling companies that process rubble into road construction granulate. For the time being, this remains a lucrative business, witness the number of recycling plants that have seen the light of day since 1995. They get paid both to take in debris from the demolishers, and to supply granulate. But the time is nigh when the demand for road construction granulate will decline as fewer new roads are being built, and the concrete industry 'demands' the concrete rubble fraction. This will open the road to recycling of bricks, and will even turn it into necessity."

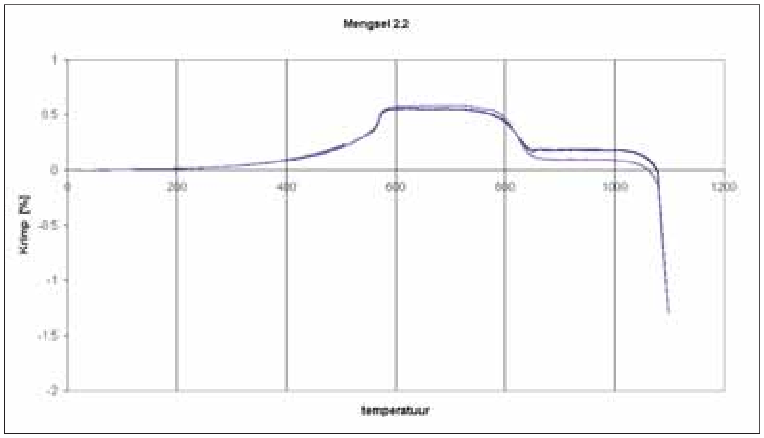


At the Kijfwaard brickworks at Pannerden, a test was conducted in which the brick fraction, after being ground, was mixed with clay in a 50/50 mix. Using the common Dutch production method with moulds (because of the soft clay), the mixture can be used to produce bricks. The clay mass is pressed into moulds that have been sanded to make the unfired bricks easier to extract.

The residual fraction, which consists of broken and damaged bricks and mortar, can be separated into pure fractions of bricks and mortar by means of magnetic separation so research at the Applied Earth Sciences faculty has shown. This is made possible by the fact that the brick particles contain about 3-5% iron, while the mortar particles contain less than 0.5%.

The unfired bricks are left to dry to the atmosphere for several days.

To prevent the ‘green’ bricks breaking during the internal transport at the factory, they must be sufficiently dried.



During the firing, the quartz contained in the material transforms from its alpha phase to its beta phase, a process associated with sudden expansion.

According to Rem however, it takes a little more than that: “No company in the world is going to launch a product for which there is no market yet, hoping that the rest of the chain will follow suit. To close the cycle will require a coherent infrastructure.” Which is why TNO-MEP, together with seven companies from the chain are working on a method to further develop the concept of a closed material cycle for concrete and masonry.

Guarantees ¶ It is not to be expected that the government will force the reuse of bricks.
Rem: “The trend is to loosen legislation and to increase the responsibilities of the market parties. This is a deathblow to innovation. The problem lies in accountability. If in ten years’ time, recycled bricks are found to develop cracks, the builder will be held responsible. The risk simply does not outweigh the cost saved by reuse. The government is the only party that can accept such a responsibility, for example by issuing some kind of product certificate.”
Whether the market will use these bricks depends not only on the quality of the bricks, but also on their aesthetic qualities, which may be affected by their slight grey bloom.
“They may well become a success if architects introduce a recycling look instead of bright red,” says Van Dijk. Even so, Van Dijk is certain that there is a bright future for his invention, and he is eagerly following developments. There is little more to do when you develop a solution to a future problem. He now works as a civil engineering consultant at KH Engineering in Schiedam, where he does calculations on various industrial steel and concrete structures. In addition, together with Edwin Swart, who did his doctorate research at the same time as Van Dijk, he runs an architectural and civil engineering consultancy firm, Van Dijk & Swart B.V. where they calculate and design building structures.

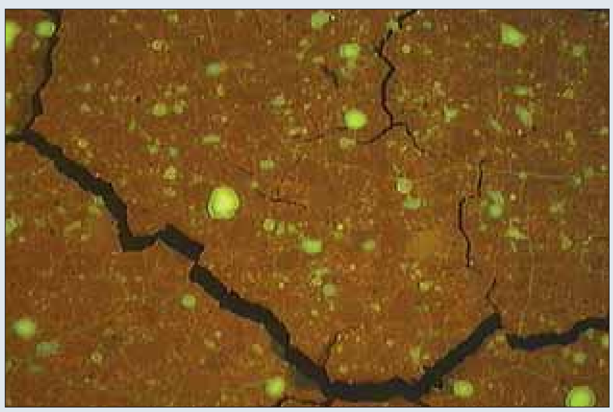
For more information, please contact Ir. Koen Van Dijk, phone +31 10 2088757, e-mail mail@avds.org, or Prof. Dr. Ir. Charles Hendriks, phone +31 15 2787439, e-mail ch.f.hendriks@tudelft.nl.

The newly fired fifty/fifty bricks containing 50% brick granulate and 50% clay.

From left to right: the reference brick (pure clay), the fifty/fifty brick containing 50% masonry granulate, and the fifty-fifty brick with 50% brick granulate.

The surface assumes the colour of the fired clay, whereas the sections show brick particles of different colours. The sections have been injected with resin to produce strong polished samples that can be viewed through a microscope.

If the temperature treatment during the firing is rushed, the inside of the product can end up cracked, which affects the mechanical quality of the brick.



Margarine, the interface between bread and filling, is made of mostly vegetable oils. To harden the oil to make it spreadable, it is treated with hydrogen in a 3-phase reactor. This catalytic process has to be kept within tight limits in order to keep the amount of saturated oil acceptable. This is just one example of the many products produced in slurry-bed and fixed-bed reactors.

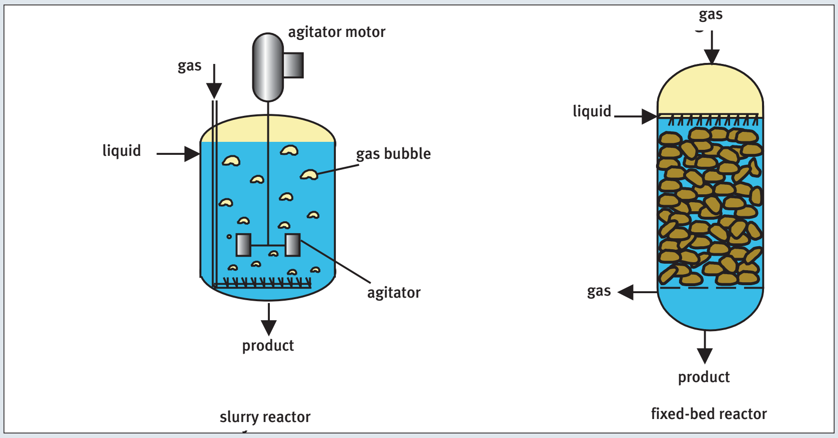
Monolithic reactor: higher yield, less energy

An unexpected bonus for the industry thanks to a new type of reactor

by BENNIE MOLS

The production of margarine, the desulphurisation of crude oil, and the manufacture of synthetic diesel fuel, these are only three of the many industrial processes in which a three-phase reactor is used. Traditionally, this type of reactor is rather ill-defined. Success with a lab scale set-up is no guarantee that a large commercial reactor will work. Scalability is less than perfect, one might say. Researchers at the Reactor & Catalysis Engineering department of the Chemical Technology faculty at TU Delft have now developed a new type of reactor that is well-defined and nicely structured, making it highly scalable. And as an unexpected bonus, the yield increases as the energy fed to the system decreases, which is quite the opposite of what takes place in traditional reactors. The secret is in catalyst blocks with thousands of narrow, parallel channels, feeding gases and liquids at exactly the right rates, and presenting the initial flow in the right manner.

The industry uses many reactors in which a gas, a liquid and a solid all play a role. These are called three-phase reactors. Companies such as Unilever, Shell, DSM and Akzo all work with them. Inside a three-phase reactor the gas often



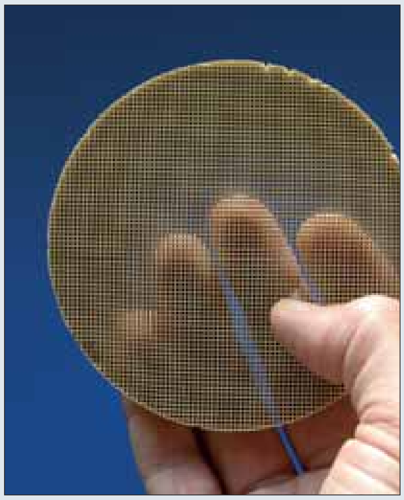
Section through the classic 3-phase reactors. On the left is an agitated vessel, in which the gas and the powdered catalyst are beaten through the liquid by an agitator. In the fixed-bed reactor, larger catalyst particles are dumped in the vessel, after which the gas and the liquid trickle over them. Both types of reactors are common in the foodstuffs industry, in the classic, large-scale petrochemical industry, in the pharmaceutical industry and in purification plants.

Classic fixed-bed reactors operate with catalyst granules the size of rice grains, although other forms exist, such as spherical or disc-shaped granules. In the centre are some ceramic structures with parallel straight channels of the type used at TU Delft. The fine structures enable a well-defined reactor to be developed in which the interaction between gas, liquid, and catalyst can be predicted with high accuracy. The catalyst is applied to the ceramic structures by means of a number of different processes.

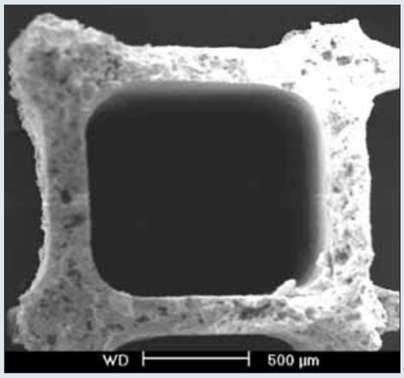
used is hydrogen or oxygen. The liquid is frequently something produced by the petrochemical or organic chemical industry. In most cases, the solid acts as a catalyst, a material that speeds up the reactions without being deformed or consumed. A three-phase reactor is at the heart of the production of margarine from vegetable oils with hydrogen gas, to take one example. Hydrogen gas and a liquid vegetable oil flow into the reactor, and liquid margarine comes out. The hydrogen is consumed in the reaction at the catalyst surface. The desulphurisation of crude oil with hydrogen gas also takes place in a three-phase reactor, as does the production of synthetic diesel from a synthesis gas.
Three-phase reactors come in two different types. In a fixed-bed reactor, the gases and liquids flow through a stationary solid phase, a bit like water and air flowing through a bowl of rice. The other type is the slurry reactor, in which the solid phase consists of fine powder particles that move along with the liquid. Both types have their pros and cons. Fixed-bed reactors tend to be slow in transferring the reactants to the catalyst, since the flow rate of the gas/liquid mixture through the reactor is low. The drawback of slurry reactors is that the fine catalyst powder must be carefully filtered out of the product. On the other hand, the close contact of the reactants with the catalyst particles makes for a high mass transfer rate.

Badly defined ¶ Both types of reactors share a drawback, which is that they are badly defined. In a traditional fixed-bed reactor, the particles can block each other's way, or stick together in random configurations, making it impossible to perform fundamental calculations. A slurry reactor is also badly defined, with too many parameters such as energy consumption and heat and reactant transfer rates being interlinked, making it impossible to upscale a small test model into a full-size production reactor. In a large reactor, additional problems occur, such as large vortices in the liquid that don't occur in small-scale operations.
In reactor science, scaling is a science in its own right.
"We would like to rid reactor science as much as possible of the badly defined reactors," says Michiel Kreutzer, who recently gained his doctorate at Delft University. He studied chemical engineering at Groningen University and did his degree work at DSM, Geleen. "There are whole books full of empirical correlations. Most of them are useless for scaling up a process," says Kreutzer. "Either they apply to a limited range, or they have been designed to apply say to only a mixture of air and water, making them totally unsuitable for other gas/liquid combinations."
This drawback provided a major incentive for research into so-called monolithic structures. An example of such a monolithic structure is the catalytic exhaust converter attached to most motor cars these days. It is a ceramic structure consisting of thousands of parallel, one-millimetre square channels. It is a beautifully ordered, self-repeating structure that is capable of withstanding the rapid temperature changes that occur in automotive applications. The ceramic carrier material is coated on all sides with a layer of catalyst that converts the noxious particles in the exhaust gases into less harmful substances. This makes the monolithic catalyst used in cars one of the most widely used chemical reactor, although it is a gas/solid reactor and not a three-phase

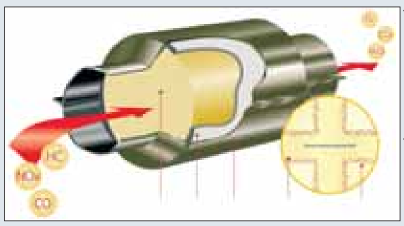
Two bottles of slurry catalyst. The bottle on the left is filled with heavy, relatively fast-settling particles. The bottle on the right contains a very fine powder that takes a very long time to form a sediment. The long settling time makes the powder less useful.



As this monolithic ceramic clearly shows, an open structure with thin walls forms a negligible obstacle to the fluids flowing though it. As the channels are so narrow, the result is a large surface area for the reactants to come into contact with the catalyst.

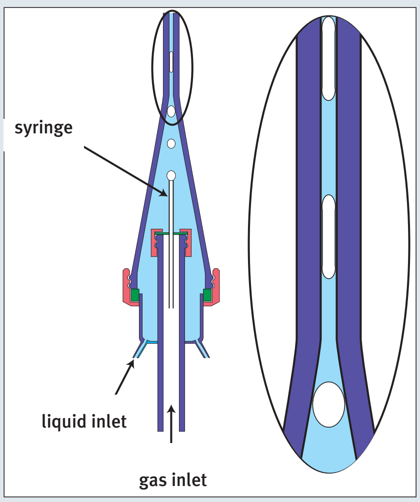


This electron microscope view shows a monolithic channel to which a catalyst coating has been applied. The coating has filled the original sharp angles (see bottom right-hand corner). Since only the top few micrometres of the coating are involved in the catalytic process, new coating techniques can offer considerable savings on catalysts such as palladium, which are often expensive.



(IMAGE: CORNING INC.)

The breakthrough in the development of catalytic converters for cars was the use of monolithic structures that, contrary to fixed-bed reactors, require only a negligible fraction of the car engine's power to push the exhaust gases through the reactor.



Dr. Kreutzer designed a glass single-channel set-up in which the process can be observed as it happens to obtain the best possible insight. The crucial factor turned out to be the length of the bubbles and the slugs of liquid between them. In cooperation with the glassmakers at TU Delft he developed an inlet system in which the bubble length could be varied with great accuracy by changing the thickness of the gas injector syringe.

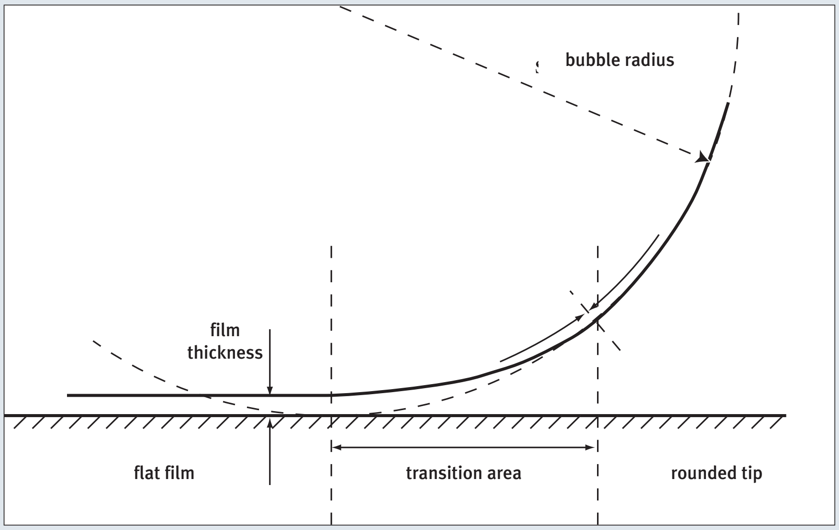
In addition to research into flow behaviour of gases and liquids in monolithic structures, the department of Prof. Jacob Moulijn also investigates chemical applications. For this purpose, small samples are coated with a catalyst. The samples are then placed in an annular holder in which an Archimedes screw is used to pump gas and liquid through the samples. This way the monolithic structures can be tested for various chemical applications using a minimum of expensive catalyst (typically precious metals such as platinum or palladium) and reactants on a small scale.

reactor. The main advantage of a monolithic reactor is its regular, well-defined structure.
"The flows inside traditional three-phase reactors are very badly defined. On the other hand, the flow inside a single monolithic channel is extremely simple. There are no problems with turbulence, everything is nice and laminar. They are easy to perform calculations on, too, making them easier to design, and you can test as many liquid combinations as you like in a numeric simulation, whereas an experiment would take much longer. This means that you can do calculations for any number of gases and liquids", says Kreutzer at the department until recently known as Industrial Catalysis.

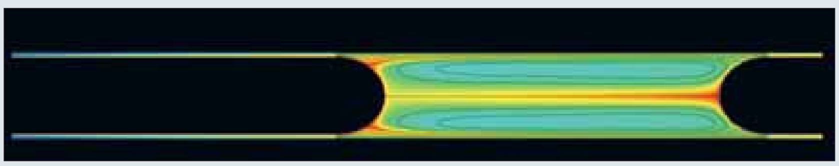
From exhaust gas to margarine ¶ About a decade ago someone came up with the idea of using monolithic reactors for gas/liquid mixtures in industrial processes instead of using them exclusively for gases, as car exhaust converters are. However, practical application proved far from simple. The first experiments carried out in Sweden and the United States resulted in chaotic flow patterns. The gas and liquid were pumped upwards through the channels of a vertical column of monolithic material. Some channels were found to contain only gas, while others contained nothing but liquid, precluding any reaction between the gas and liquid phases. Some of the liquid stayed inside the monolithic structure for quite a while, whereas some emerged soon after entry. All in all, not much of a structure. The conclusion was soon drawn that this flow pattern, from the bottom upwards, was unstable.
Would a top-down flow perform better? Again, the first tests indicated an unstable flow pattern. Nevertheless, Prof. Dr. Jacob Moulijn of the Reactor & Catalysis Engineering department felt that better results could be obtained. And so Michiel Kreutzer started his research for his doctorate under Moulijn's supervision.
"I was asked to find out what makes up the flow inside a monolithic reactor, insofar as relevant for reactor science," Kreutzer explains. "When we started, we thought we knew everything there was to know about the flow in a single channel, and that all we would have to do was to scale up to multiple channels. After a year of experimental and numeric work, however, we discovered that we were going to have to totally readjust our ideas. Everything we thought we knew turned out to be wrong. Most of what we now know, we learnt from the experiments in a single monolithic channel. Once you have that well and truly covered, you can start to try to understand a structure with thousands of separate channels."
Kreutzer used both computer simulations and experiments to look into the behaviour of the gas/liquid flow in the monolithic structure. Essential parameters include the loss of pressure between the inlet and outlet, the flow pattern, and the mass transfer of reactants towards the reactor walls. These walls are coated with a thin layer (about ten micrometres, which is one-tenth of the thickness of the wall) of catalyst material, usually a combination containing elements such as aluminia, platinum, and palladium.
"The manufacture of a catalyst is a very specialised field," Kreutzer explains, "which I did not go into. Fortunately our department is looking at practically every aspect of these reactors. Others in our group can tell you everything you need to know about the catalyst material. My job was to look at the flow

Different flow patterns can occur in gas/liquid flows inside channels, including large bubbles, small bubbles, and foams. In capillary tubes, a bubble train flow pattern results, consisting of elongated bubbles separated by slugs of liquid. Inside these narrow channels, the capillary forces are so dominant as to enable the bubble to push practically all the liquid ahead of it. Between the wall and the bubble there is only a very thin film, which hardly forms any obstacle at all to the gas diffusing towards the wall.

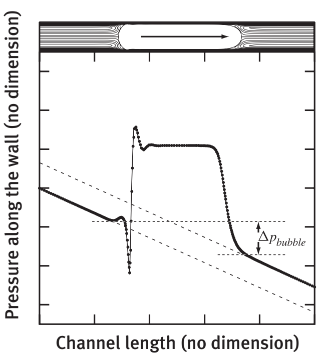
The behaviour of a bubble train can also be calculated very well with a computer. These simulations not only confirm the experimental results, they also yield a wealth of extra information. For instance, a circulation has been found to occur inside the slugs that continuously transports components from the centre of the channel towards the wall, as can be seen from these calculated



The area between the round tip of the bubble and the thin film is called the transition area. In it, the relative strength of the capillary forces (which push in the direction of the wall) and the viscous forces in the liquid (which oppose the pushing action) determine the thickness of the film. Theoretically, a simple deduction can be made to show that, as the rate of flow increases, the effect of viscosity increases. Conversely, as the flow rate decreases, the film gets thinner, and the rate of mass transfer increases.



After Kreutzer had calculated the flow field, he focused on the transport of reactants inside the channels. This figure visualises the dissolving of oxygen in a channel containing water. The colour indicates the degree of saturation. At the ends of the bubble, oxygen is continuously being absorbed. The circulation of the liquid is reminiscent of a caterpillar track crawling along the channel wall. The movement also ensures that the dissolved gas passes directly along the catalyst on the wall, where it can participate in the reaction. This is one of the reasons why monolithic structures perform so well.



Even though the pressure differential in monolithic reactors is small compared to other types of reactors, it remains crucially important to know exactly how high the pressure drop is, since it affects hydrodynamic stability of the reactor. Roughly speaking, there is a constant pressure drop at the slugs, and no pressure drop at the bubbles, as can be seen from the sloping lines in the graph. However, the pressure drop along the total length of the bubble is not zero, as the horizontal dotted lines indicate (ΔP_{bubble}). As it turned out, this pressure drop proved crucial for predicting the limits within which a monolithic reactor remains stable in operation.

patterns inside the monolithic reactor.”

Before Kreutzer started his research, it was thought that to obtain a stable pattern in a downward flow, the average velocity of the gas/liquid mixture would have to be about twenty centimetres per second, although even the very existence of the stable flow pattern was questioned. In order to ensure that the reactants remain inside the reactor for long enough to actually react, a velocity of twenty centimetres per second would rapidly result in a commercial reactor with a height exceeding five hundred metres. In other words, totally impractical. The new results were just what we needed.

“Our results showed that you can reduce the velocity down to only three or four centimetres per second. This means that a much more compact reactor can be used in which the reactants get to remain the same time inside the monolithic structure.”

Improved transfer with less energy ¶ Inside every reactor, the gas and the liquid ultimately have to find their way into the porous material of the catalyst, in which the actual conversion takes place. In monolithic structures, the catalyst material sits on the walls of the channels. That is where the desired end product, usually some kind of liquid, is formed. The crucial question is what type of flow pattern will get the gas and liquid molecules to the wall in the shortest possible time. The typical flow pattern inside a single narrow monolithic channel is what is known as Taylor flow, in which large gas bubbles with an elongated nose and a flattened rear are separated by slugs of liquid, called slugs. Inside a slug, the liquid circulates like a caterpillar track, enabling liquid molecules to reach the wall not only by diffusion (a process involving random collisions between molecules without any induced direction, and therefore slow) but also by much faster convective transport. A thin film of liquid separates the elongated gas bubbles from the wall. As the film becomes thinner, it becomes easier for the gas to diffuse through the film towards the wall. The ideal film thickness is something like a few micrometres. The only parameters open to variation by process technologists in actual practice are the inlet flow rates of the gas and the liquid. In most industrial reactors the reactant transfer rate increases with the amount of energy fed into the reactor. Stir harder and you will get better mixing. But not in monolithic reactors.

“The most unusual, and at the same time counter intuitive finding of my research,” Kreutzer says, “is that in a monolithic reactor the reactant mass transfer rate increases as you reduce the amount of energy dissipated in the system.”

Less energy translates into reduced inlet flow rates.

“Every time we submit our findings to a company, they refuse to believe us at first. ‘Nature does not give presents’ is what they say. But if you think about it, you can see the logic of it all. As you increase the flow rate of the input liquid, you increase the thickness of the film between the bubble and the wall. A thicker film makes it harder for the gas molecules to penetrate the liquid film and reach the catalyst-coated wall.”

A reduced flow rate results in a thinner film, thus improved reactant transfer. However, if the flow rate is reduced too far, the monolithic structure becomes unstable. This means that the flow rates in a real process must be close to instability, i.e. keep the flow rate as low as possible without exceeding the limits of stability. Fortunately, monolithic structures proved to be must more stable at low rates of flow than previously believed.

“It took some time before I could believe the evidence myself,” Kreutzer says, “but the findings resulted from experiments as well as computer simulations. It is important though to have a good gas/liquid distributor that creates the right inlet conditions. We were presented with what you might call an unexpected present from nature: lower energy consumption and improved reactant transfer rate. We have now provided a fundamental demonstration of the fact that our monolithic reactor can be used on an industrial scale.”

Round versus square ¶ Current monolithic structures use channels with a square section. Another finding of Kreutzer’s research is that a circular section would be ideal. Round channels result in a liquid film with a lower average thickness, and consequently, an even better reactant transfer rate, probably up to three times as good.

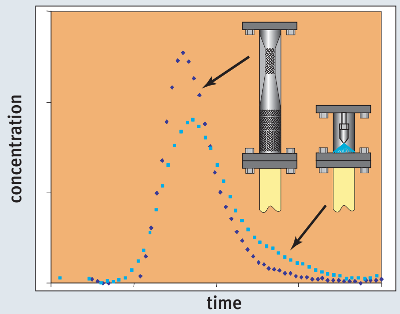
“We have been in contact with a manufacturer of hexagonal-section monolithic structures, which are closer to the circular shape and should result in a marked improvement over the square section structures.”

Shower head used as a distributor.

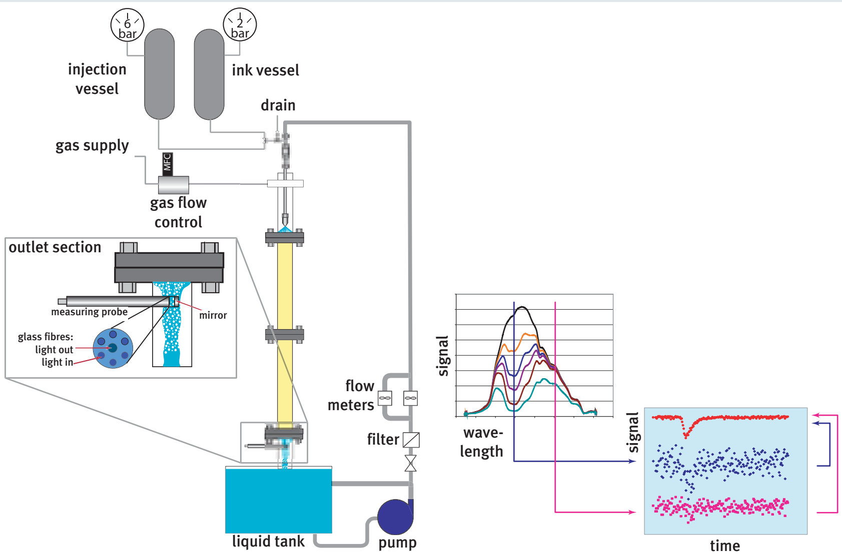
Tap point for measuring oxygen concentration.

The oxygen is removed at the bottom end of the test set-up before the liquid re-enters the column

Following the accurate experiments in a single channel, the time came to look into the feasibility of monolithic structures on a semi-industrial scale. The pressure differential and the absorption of oxygen in monolithic structures were mesuared in a 10 cm wide column. Even though such a column cannot be compared with an industrial column more than a metre in diameter, scaling the process from one to many thousands of channels gave Kreutzer much better insight.



The experiments started with a simple household shower head and it soon emerged that a better gas and liquid distributor was required. A number of different distributors were developed. These were tested in experiments by injecting a droplet of ink through the distributor into the channels and measuring how long it took for the ink to emerge from the channels. If the ink traces emerged at more or less the same time, this indicated that the flow through each of the channels was similar. The difference in the time it takes to pass through the system is referred to as the residence time distribution. Such experiments are relatively inexpensive yet offer sufficient evidence for selecting the distributor on the left over the one on the right.



Test set-up for measuring the residence time distribution. The problem with the ink-in-water method is that the liquid contains gas bubbles at the outlet (where the readings are taken). These bubbles make it practically impossible to directly measure the ink concentration, since light is diffracted as soon as it hits a gas-liquid interface. Separating the gas from the liquid for the measurements proved to be impractical, since the separator had a residence time distribution many times greater than that of the channels themselves. Kreutzer came up with a solution, together with Avantes (a company manufacturing optical equipment). Six optical fibres illuminate a mirror that reflects the light onto a collector fibre in the centre. Although some of the light from the six fibres will not reach the central fibre, the remaining light will manage to pass through the bubbles unchecked. The liquid concentration directly below the column could be quickly and accurately measured by combining two wavelengths from the reflected spectrum.

To find out whether the flow behaviour inside a single channel is representative for a flow through many parallel channels, Kreutzer looked into the resident time distribution of the liquid elements. The residence time indicates how long a certain liquid element spends inside the reactor. If different liquid elements have greatly varying residence times, the resulting range is large. If they differ hardly at all, the residence time range is small.
"A small residence time range is desirable," Kreutzer says, "since it indicates that by and large the channels behave identically."
He tested the residence time by injecting a coloured dye at the inlet side of the reactor and measuring the time it took for the various dye elements to emerge at the bottom end. The results indicated a relatively narrow residence time range.
Some researchers these days can use MRI scanning equipment to see what happens in each channel in a single shot, but it is a very expensive method. "The dye method is extremely cheap and reliable to boot," the researcher says. "The great thing about flow dynamics is that simple rough-and-ready methods will get you a long way."

Conservative ¶ The fact that the residence times of the various liquid elements differ hardly at all, improves the chances of success for scaling up the monolithic reactor from a single channel to several thousands of channels. However, for industrial use, the monolithic reactor must become must wider and longer than Kreutzer has been able to test. Although the channel width within the monolithic structure remains the same, large-scale applications involve the use of several tens of thousands of parallel channels rather than a few thousand.
"Our medium-scale experiments are the best we can do within the restrictions of academic research, but they are sufficient to show the industry that monolithic reactors offer great benefits in gas/liquid reactions. Scaling up the experiment even further would be too costly for us due to the large amounts of chemicals required."
The main consequence for industrial use is that the Delft design results in a monolithic reactor that is a fixed-bed reactor with the benefits of a slurry reactor, but with much lower energy consumption. Since low inlets flow rates even help improve the reactant transfer rate, the reactor can be relatively compact and still offer sufficient residence time for the reactants.
"I expect it will take another decade or so before this results in an established technique," says Kreutzer. "Constructing a true size pilot plant costs a lot of money. This makes the chemical industry inherently con can be absolutely sure that it will work."

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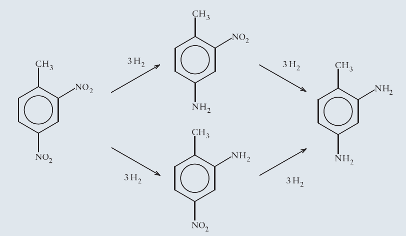
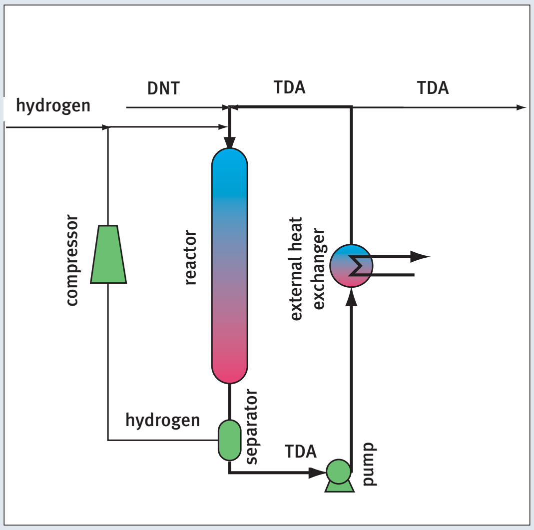
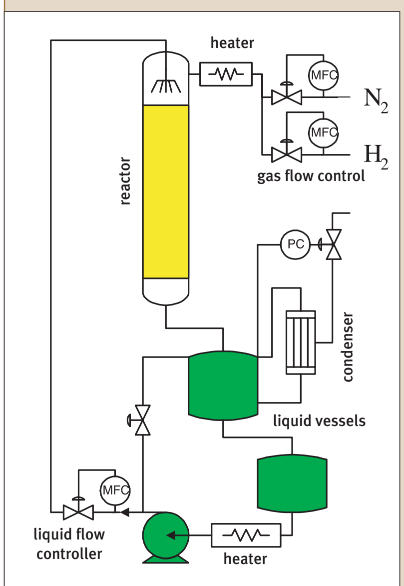


Air Products B.V. has obtained a patent on a 3-phase process in monolithic structures for the processing of a substance similar to the explosive TNT. Its applications include the production of polyurethane foam. Using a mathematical model of the process, Kreutzer was able to reproduce the patent data using the design equations from his research. In the process, DNT (dinitrotoluene) is combined with hydrogen to form TDA (toluene diamide). The nitrous compounds used in the process react very rapidly with the hydrogen inside the channels, producing a large quantity of heat. A liquid circulation system connecting the reactor to a heat exchanger is used to extract the heat. In a separate circuit, hydrogen gas is pumped round. To keep the temperature low (for reasons of safety), a little DNT is added to the liquid circulation at a time. The result is that the product has to circulate through the reactor dozens of times. As the TDA product gets pumped around, it acts as a heat buffer between the reactor and the heat exchanger. The monolithic reactor, with its high reactant transfer and limited pump capacity requirement, is eminently suitable for a circulation process of this kind.



The pilot plant

Before a chemical company can put their trust in a new type of reactor developed by a university, they will want to see a reactor that is as close to industrial scale as possible. However, an industrial-scale reactor is a financially impossible goal for a university. To convince the industry that the monolithic reactor has a large-scale commercial future, researchers at the Reactor & Catalysis Engineering department constructed a medium-scale test reactor to which the industry is happy to contribute.
The Delft test reactor consists of stacked monolithic blocks of up to two metres high. These are surrounded by the inlet and outlet pipes that carry the various gases and liquids. In small-scale experiments as well as in this medium-scale pilot plant, the researchers have demonstrated that the mass transfer rate in the monolithic reactor increases as the inlet flow rate of the reactants decreases.
"At first sight it is a counter-intuitive finding," says Dr Michiel Kreutzer. "Using the pilot plant, we are able to integrate the department's knowledge of fluid dynamics with the knowledge in the field of chemical catalysts. On open days, secondary school pupils and their parents are amazed when they see this reactor, which is pretty hefty as far as university reactors go."



Test plant overview

Reactor

Gas/liquid separator

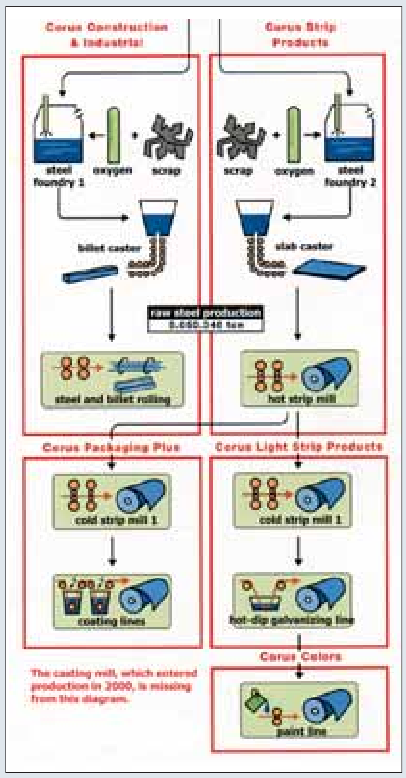
A 'living' material that does not easily reveal its secrets.

X-ray view of steel

At the Corus IJmuiden mills, steel at 1200 °C is rolled at high speed to the desired thickness in a number of steps, then cooled with water.

by ARNO SCHRAUWERS

Steel is a difficult material, or rather, it tends to guard its secrets jealously. At the Interfaculty Reactor Institute (IRI) and the subfaculty of Materials Science and Engineering at TU Delft, Dr. ir. Erik Offerman is doing his utmost to get to the bottom of this enigma. His endeavours even required the support of the synchrotron of the European Synchrotron Radiation Facility (ESRF) at Grenoble in France. Using an X-ray beam from this electron accelerator – which is about a billion times as strong as the types used in medical X-ray equipment – he managed to become the first person to actually observe the changes in steel as they took place, an achievement that got him into *Science* magazine. In the mean time, Offerman has developed a model that will enable him to explain the observations made at the synchrotron in Grenoble.



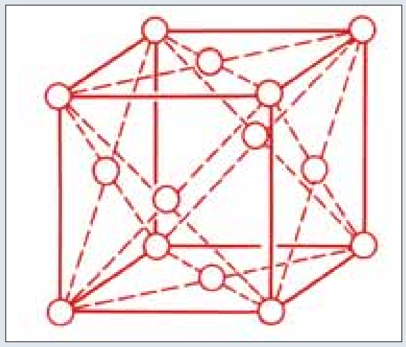
Schematic diagram of the steel production process at Corus IJmuiden that processes scrap metal into a range of end products.

Steel remains the most widely used structural material, with properties that make it a clear favourite for a wide range of applications. However, steel is also a difficult material. The reason for this is that steel is an alloy, an amalgam of various elements, with iron and carbon forming the basic ingredients. To a large extent, the properties of a steel alloy are determined by its microstructure, i.e. the way in which various crystals that make up the solid material are shaped and connected. These crystals can be seen through a microscope, where they present a rather complicated view. The size of each crystal depends on the alloy components and, more importantly, on the way the steel is cooled after the rolling process at high temperature. The components making up a steel alloy vary and can include manganese, silicon, aluminium, chromium, nickel, molybdenum, and phosphorous.

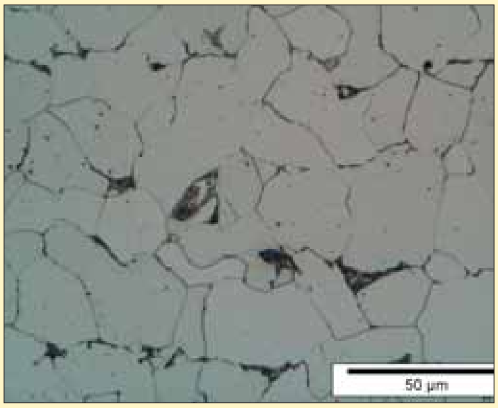
The microscopic structure of steel can occur in a number of different crystalline forms, the most important of which are austenite and ferrite, both of which are ductile. In addition there is pearlite, which is layered but strong, the needle-structured bainite, of intermediate hardness, and the strong but brittle phase called martensite. Not to worry, we are not about to embark on a course in crystallography. This is just a basic introduction to make Offerman's story easier to follow and to help you understand why the various forms of crystals in steel ultimately determine its uses.

(PHOTO: ERIK PEEKSTOK, DELFT)

Microscope view of austenite in pure iron. The image was obtained using a laser-scanning confocal microscope at a temperature of 1000 °C.

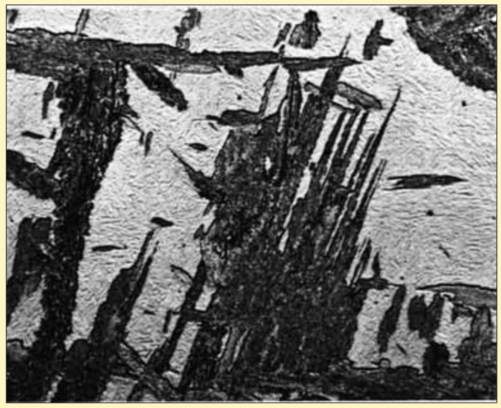


Crystal structure of austenite in pure iron. Austenite is stable at temperatures over 912 °C. The iron atoms are arranged in a regular pattern at the vertices and in the centres of the six surfaces of an imaginary cube. The structure is known as face-centred cubic.

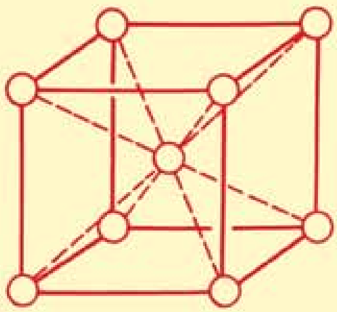


Optical microscope image of carbon steel at room temperature. The pale grey areas in the microstructure are ferrite crystals separated by crystal boundaries (the black lines). The large black areas are colonies of pearlite. The small black dots are impurities that are always present in commercial steel.

(PHOTO: TON DE HAAN, DELFT)



Optical microscope image of bainite (dark areas) at room temperature. Like pearlite, bainite is a composite of ferrite and cementite, but it has a totally different microstructure. Bainite consists of ferrite needles interspersed with cementite.

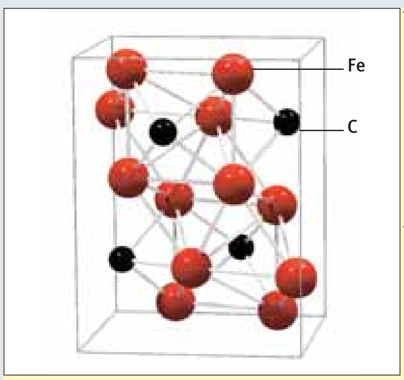


Crystal structure of ferrite. The iron atoms are arranged in a regular fashion at the vertices and at the centre of an imaginary cube. The structure is also referred to as body-centred cubic.

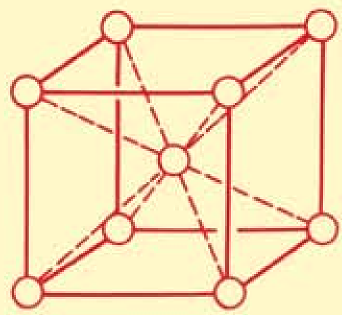
(middle above) Optical microscope image of practically pure perlitic steel at room temperature. The Pearlite structure consists of alternating layers of ferrite and cementite (Fe_3C).

BMW ¶ 'There is a trend towards producing types of steel that combine high strength with a high degree of formability,' says Offerman, who recently gained his doctorate with professor Dr. ir. Sybrand van der Zwaag, 'and in order to be able to control the manufacturing process, you need to know exactly how the crystals grow. The most important process in the production of steel is the transformation of austenite into ferrite, and to a lesser extent, into pearlite. At high temperatures, austenite takes the upper hand, but at room temperature you tend to get ferrite. The formation of new ferrite grains from existing austenite grains was the basis of my research project at ESRF. Steel with a high ferrite fraction forms the basis of most types of steel used in applications requiring high strength and formability, such as sheet metal for car bodies. In addition, there is austenitic steel, in which the austenite is stable at room temperature.'

The advantage of this is that austenite produces extremely strong yet highly formable types of steel. On the other hand, austenitic steel types are expensive because they require relatively large quantities of high-cost alloy elements. The industry is currently working on a cheaper alternative, TrIP steel (in which TrIP stands for Transformation Induced Plasticity). The composition of this type of steel is very similar to that of the cheapest carbon steel types, but special



(IMAGE: MARNIX WAGEMAKER, DELFT)

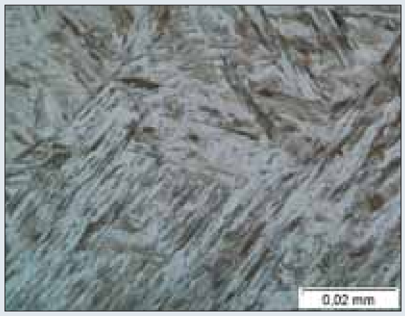


A colony of pearlite consists of two interwoven crystals, cementite (left) and ferrite.

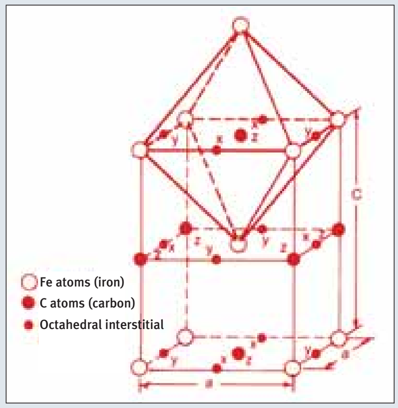
heat treatments and the addition of aluminium, silicon, and phosphorous result in a special microstructure containing about 10 percent of residual austenite. The moment a piece of TrIP steel is deformed, the residual austenite is instantly transformed into martensite which increases the strength of the material and failure is delayed.
Offerman: 'This type of steel is of interest to upmarket car manufacturers, such as BMW. TrIP steel is first subjected to a special heat treatment in which the steel is heated to 800 °C, a temperature at which both austenite and ferrite co-exist. The material is then rapidly cooled to 400 °C, causing part of the austenite to be converted into bainite, while the rest of the austenite remains intact, even after cooling down to room temperature. The hard X-ray technique I have used to look at steel is eminently suitable for observing such processes as they take place. While my research so far has focused on the transition from austenite to ferrite, plans exist to take a look at bainite as well. The ultimate goal is to produce tailor made steel .'

Gun target ¶ So what about the actual research? During his research for his doctorate, Offerman looked at steel samples at various temperatures using X-rays from a synchrotron, which is a particle accelerator that can supply very high-intensity, very high-energy X-rays. Bombarding a steel sample with these hard type of X-rays from the synchrotron produces a plot – a spectrum – that looks like a target at a gun range. In this case the dots on the target aren't bullet holes, but provide information about the crystals that make up the steel sample. By zooming in on these holes, you can see the crystals grow and decay as it were. Once you really get to know the differences between austenite and ferrite, the method enables you to follow the nucleation and growth of ferrite crystals and the disappearance of the austenite crystals.
Put like this it all seems very simple, but Offerman and his fellow team members were the first people to ever observe these processes live. It has to be said though, that in order to be able to do so, Offerman worked in close cooperation with Dr. Henning Poulsen, Dr. Erik Lauridsen, Dr. Larry Margulies and Dr. Stephan Grigull, all staff at the Danish Risø National Laboratory research centre at Roskilde. They were the ones to develop the beam line of the synchrotron that Offerman used for his measurements. They also wrote many of the computer programs that process the experimental data into bite-size units.

Models ¶ Yet another bit of theory about steel: in order to understand the transition from austenite into ferrite, it is essential to know that ferrite can contain less carbon than austenite. In other words, the crystal lattice of austenite offers a hundred times as much room for carbon as does the ferrite crystal. This is why, when ferrite is formed, carbon gets ejected from the ferrite grains, which is the preferred term among the researchers when they mean crystals.
Offerman distinguished four types of growth for the ferrite crystals, the occurrence of which depends to a large extent on the amount of ferrite already formed in the parent austenitic environment. The first type of growth is called as the Zener growth, named after professor Zener who as early as 1949 had indicated how the crystals grow as the temperature changes.
'In fact,' Offerman says, 'this type of growth occurs only in cases where no ferrite grains have formed in the direct vicinity. The second type of growth is one in which at one point ferrite grows on to become pearlite, which has a lamellar structure. We were the first group to make a live observation of this type of growth in three dimensions. The third type of growth is what we have named «retarded growth». The deviation from Zener's prediction is caused by the vicinity of other ferrite grains, all of which are trying to release their carbon. This slows down the nucleation of new ferrite grains.'
The fourth type of growth is what Offerman for want of a better word has named complex growth. In this process, the ferrite grains both grow and shrink. The live observations last year resulted in a publication in *Science* magazine.
Offerman: 'Even so, at the time we did not understand why these types of growth do not follow Zener's theory. We have now got to the stage where we have come up with suitable explanations for these phenomena. I have created a model that describes three of the four growth types. The most important aspect of the model is that there is a transition from non-overlapping to overlapping carbon fronts. This means that at the interface between austenite and ferrite, a carbon front is created on the austenite side, which is pushed forward like a snow shovel. When such carbon fronts meet, the growth of ferrite is



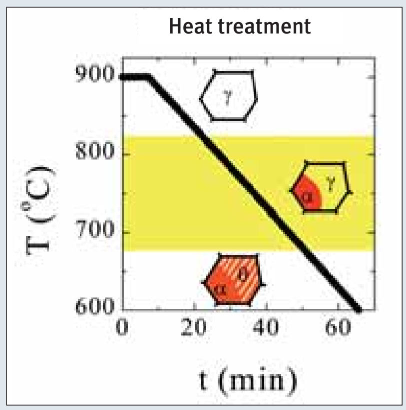
Optical microscope view of martensite at room temperature.



The crystal structure of martensite is very similar to that of ferrite. The difference is that the C-axis of the martensite crystal structure is elongated relative to the base plane (the A-axis) due to the formation process in the presence of carbon, which is frozen in the spaces between the relatively large iron atoms.

The production of steel wire at Fundia Nedsteel, Alblasserdam, in the vicinity of Rottrerdam

The cooling path of the carbon steel used for gathering the experimental data. The stable crystal phases have been schematically indicated as a function of the temperature. From high to low temperature the following crystal structures are stable: face-centred cubic austenite (γ), cubic-spatial-centred ferrite (α), and orthorhombic cementite (θ). At low cooling rates, ferrite and pearlite are formed, at higher cooling rates bainite forms, and even higher cooling rates produce martensite.

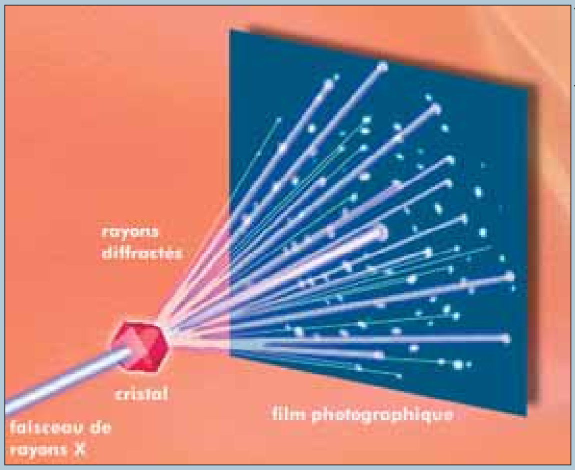


Setup at the European Synchrotron Radiation Facility (ESRF) at Grenoble

(IMAGE: ESRF)

ESRF is located on a stretch of land encircled by the rivers Isère (left) and Drac (right). In the foreground is the circular synchrotron Offerman used for his experiments on red-hot steel.

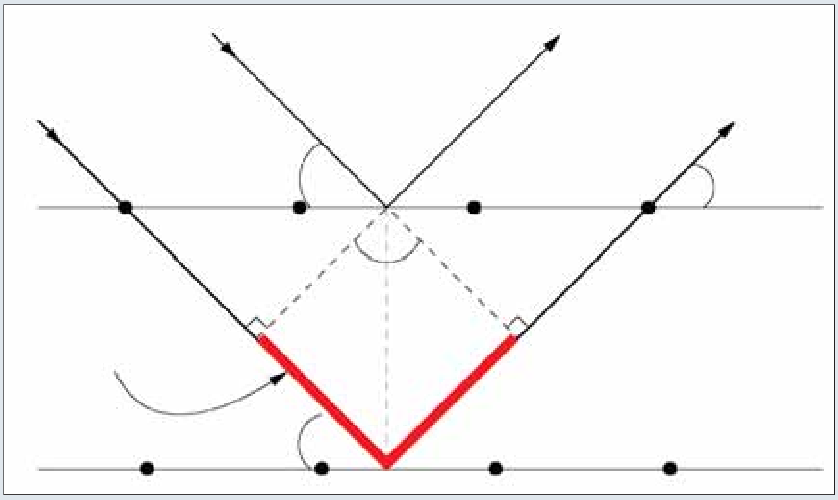
Schematic diagram of an X-ray diffraction experiment on a crystal. Radiation from a synchrotron (high-intensity X-ray radiation) strikes a crystal and becomes diffracted. The diffracted radiation is collected on a detector (a CCD camera) as a pattern of dots which is made visible on a PC display.



(IMAGE: ESRF)

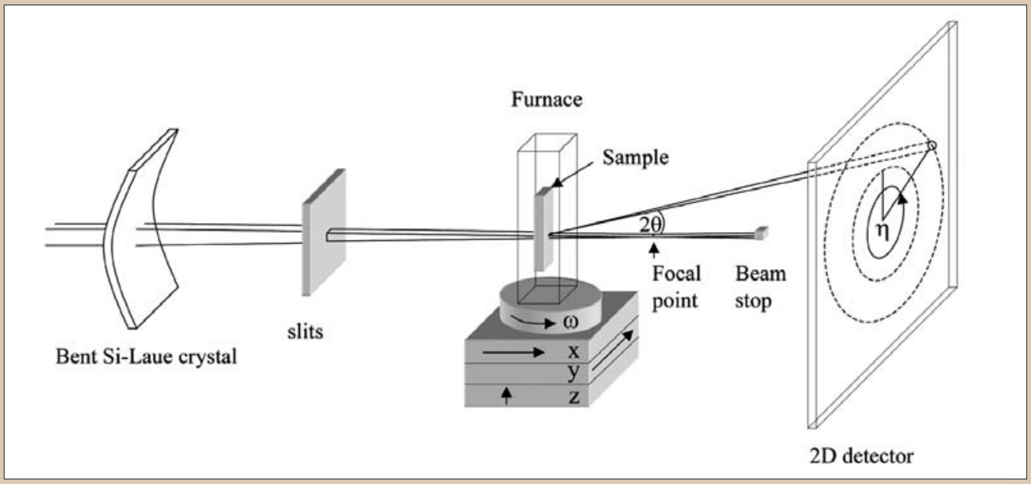
retarded. At that point, the process deviates from Zener's theory. By the way, the fourth type of growth also deviates from Zener's theory.'
This was something he did not find out until he returned from Grenoble to process the experimental data at the IRI.
Offerman: 'During the experiments at the ESRF institute we were unable to see that the cooling phase between 800 °C and 600 °C showed an oscillation in the growth of some ferrite grains. This was something I did not find out until I looked at the data back at the IRI. There are two possible explanations. The oscillation either is the result of local retransformations into austenite caused by temperature fluctuations, or it is caused by the increasing number of ferrite grains competing for the same space, a process in which the surface tension of the colliding ferrite particles plays a major role. The latter explanation would seem to be a better fit with what is actually happening, for we also looked into the disappearance of the austenite grains. We saw that the first three types of ferrite growth also occur in austenite; the fourth type does not. This makes the second theory, the one with the competing ferrite grains, more likely. The great thing about the model we are using is that we can model both the disappearance of austenite and the growth of the first three types of ferrite.'

Modified models ¶ The Delft researcher has not reached the end of the road yet. Far from it.
Offerman: 'The traditional models describe the average transformation behaviour, whereas a realistic model includes the local conditions. The growth behaviour of the ferrite turns out to be strongly dependent on the local carbon



Schematic diagram of the principle of X-ray diffraction on a crystal. At the atomic level, a crystal consists of a regular arrangement of atoms (represented here by spheres). As the X-rays (the arrows) enter the crystal and are reflected at various depths inside the crystal by the crystal planes, constructive interference of the X-rays occurs if the differences in the length travelled by the rays (red) is equal to a full number of wavelengths of the X-ray radiation.

Schematic diagram of the three-dimensional X-ray diffraction microscope used for the experiments at the ESRF. A 'white' beam of X-rays from the synchrotron, comprising a wide spectrum of wavelengths, strikes a curved silicon Laue crystal. This selects the desired 0.0155 nm wavelength and focuses the X-ray beam. A diaphragm then sets the beam size of 0.1 x 0.1 mm. The steel sample is in a furnace. To prevent detector burn-in, the centre beam is stopped by a piece of lead. The diffracted radiation is collected by a 2-D detector (a CCD camera). To date, this is the only method that has allowed the inner workings of steel at high temperatures to be observed *live*.



concentration and the number of neighbouring ferrite nuclei. If the local carbon concentration is low, with only a few ferrite nuclei nearby, the ferrite grain will be able to grow rapidly because the carbon fronts take longer to meet up.

Most models start with a single austenite grain, and assume that the carbon remains inside it during the transformation to ferrite. We have now seen that in fact this is not the case. In order to obtain a realistic description of the development of the microstructure during the transformation, the models will have to be modified. My experimental data also show that the austenite crystals tend to be rather unstable during the cooling process. It turned out that right up to the transformation to ferrite some austenite grains will increase in size while others decrease. This knowledge should also be included in the further development of models. As it happens, I am writing a paper on the subject.'

Buttons ¶ And so life as a researcher continues, with Offerman having processed only about 5% of his 100 GB of data. Even so, the processing of his data has gained momentum by now.

'I have set up a framework to process the data, and this allows me to process the data much faster than I could at the start.'

So what is the practical application of this knowledge? Where are the buttons that steel manufacturers can push to have the mills turn out the right type of steel without too much alchemy and experimentation? Isn't that what this is all about?

Offerman reassures us: 'I'm working on making these buttons as we speak. Corus, Fundia Nedsteel, SKF, and STW are paying for my first year as a postdoc to further analyse the data. During my doctorate research I had to report to my backers a couple of times a year, and they were very interested. Of course, having an article published in *Science* magazine is fantastic, but in my opinion the real proof of research is to have the results applied in the real world. The models I have developed will be particularly helpful in getting a better grip on the production process.'

As part of the Veni, Vidi, Vinci programme of the Dutch research council NWO, Offerman has been offered a Veni grant to continue his efforts to unravel even more of the steel enigma. n

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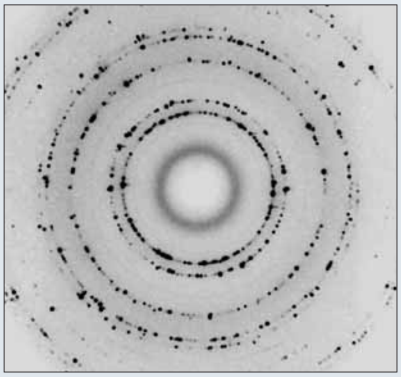
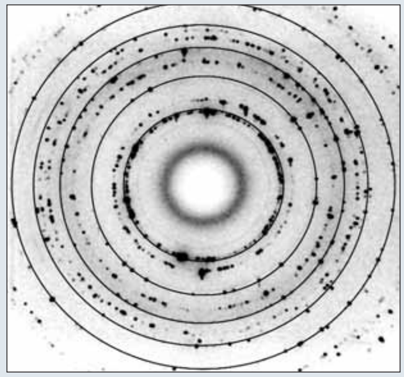
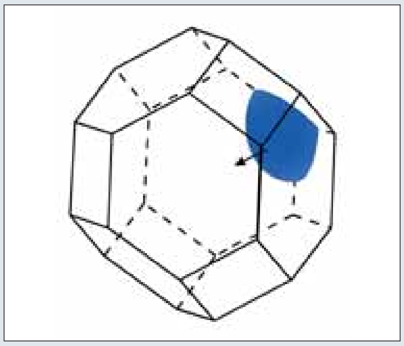


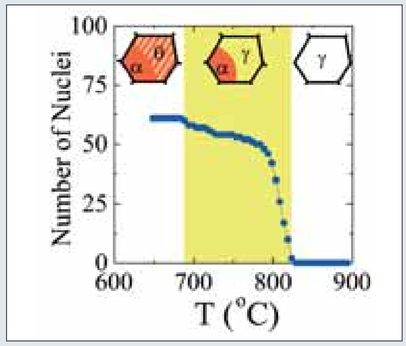
Diffraction pattern of austenite. At temperatures around 900 °C, austenite is the stable phase in the carbon steel used. The dots on the detector are all the result of the diffraction of the X-rays by individual austenite crystals within the steel sample. The size of an individual crystal can be deduced from the intensity of the dots, since a large crystal will diffract more X-rays and thus produce a higher intensity.



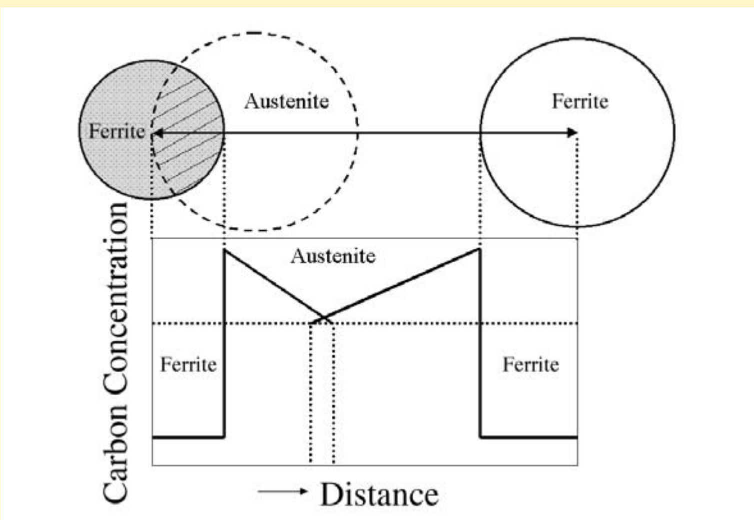
Diffraction pattern of austenite and ferrite. As the steel sample cools, the austenite crystal structure is transformed into ferrite, causing additional dots to appear on the detector (the dots on the circles). This enables the observer to see live when a crystal of the new ferrite phase is being produced. The growth of the crystal can subsequently be determined by making a film of a large number of diffraction patterns and converting the intensity of a dot into crystal size.



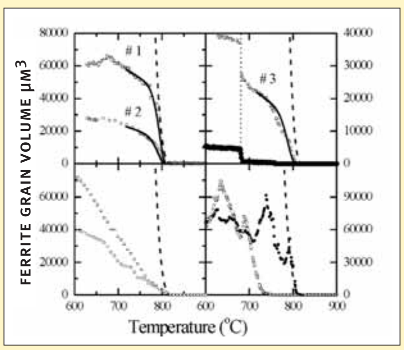
Schematic diagram of an austenite crystal with a ferrite crystal growing inside it. By preference, the crystal will start to grow on one of the corners of the austenite crystal, since that is the optimum location energy-wise.



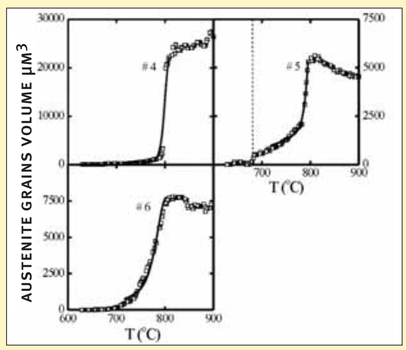
The number of ferrite nuclei measured in carbon steel that was cooled in one hour from 900 °C down to 600 °C. Offerman's measurements show that the activation energy required to produce ferrite crystals is at least a hundred times less than previously assumed. This knowledge is of crucial importance for modelling phase transformations in steel.



Schematic representation of the model used by Offerman to predict the growth of ferrite in austenite. Austenite can contain up to 2% carbon, whereas ferrite can contain only 0.02 %, one hundred times less. Therefore, as the ferrite grows, the carbon has to be pushed out in front of the ferrite crystals, which slows down the rate of growth. The growth is retarded even more by the presence of nearby ferrite grains that also try to get rid of their carbon. At a certain point, a situation occurs in which the carbon fields start to overlap.



The volume of individual ferrite crystals as a function of the temperature during the cooling process. Four types of ferrite are distinguished, the last two of which were discovered by Offerman: growth in which a transition takes place from isolated carbon fields to overlapping carbon fields, growth in which the ferrite continues to grow into pearlite at 685 °C, retarded ferrite growth due to the direct overlap of carbon fields, and oscillating ferrite growth. The broken line indicates Zener's classic growth theory, while the solid lines show the new model.



The disappearance of individual austenite crystals. Inevitably, the growth of ferrite causes the disappearance of austenite crystals. Within the disappearing austenite, although the first three types of ferrite growth (see previous illustration) can be detected, the fourth type cannot. The disappearance of the austenite leads to the conclusion that carbon atoms are being exchanged between different austenite crystals.