5 The "Food" for the Brew

5.1 Biology of Barley

Barley is likely one of the oldest plants to be domesticated by human civilization. Evidence of its domestication has been found in Mesopotamia that dates from 8500 BC. Archaeologists have uncovered an ancient village near the Sea of Galilee in northeastern Israel. Their work showed that the village burned down and was then covered by rising waters from the Sea of Galilee. Silt and clay then covered the entire site and preserved evidence of over 100 different types of seeds.

It is likely that this plant was domesticated much earlier than this. The wild barley plant, in fact, is native to the area and ranges from the Nile River into Tibet. Domestication of the wild barley (*Hordeum spontaneum*) gave rise to the barley plant that we know today.

The modern barley plant is a member of the family of grasses. The grass grows vertically and at the top of the stem rests a spike along which the barley seeds grow. When the plant matures, the spikes separate into *spikelets* containing the seeds. Two main ways in which the seeds grow along the spikelets give rise to two very important species of barley, two-row barley (*Hordeum distichon*) and six-row barley (*Hordeum vulgare*). In both varieties, the seeds grow opposite each other in long straight rows. A layer of hair-like structures known as *awns* protects the seeds.

The brewer regards the two species differently. Two-row barley seeds (also known as *corns*) tend to be larger and, because of that, they contain slightly less protein per corn than the six-row barley. However, the crop yield of the six-row species tends to be a little higher than two-row barley. In the USA, the higher protein level was desired in the production of beers with high levels of un-malted adjuncts. Thus, the six-row barley was, and continues to be, the main barley grown in the USA Two-row barley, however, produces more starch per corn and tends to be favored as the primary source of starch in the craft beer industry.

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5.1.1 The Barley Corn

The barley seed (see Fig. 5.1) consists of three main structures; the *embryo*, the *endosperm*, and the *pericarp-testa*. The *proximal* end of the barley corn contains the embryo. This structure contains the *acrospire* and *coleoptile* that develop into the above ground growth of the plant. In addition, pointing in the opposite direction are the *rootlet* and *coleorhiza* that become the roots of the plant. The embryo occupies less than a third of the total volume of the corn.

Separating the embryo from the endosperm is the *scutellum*, cells that serve to absorb nutrients from the endosperm as the seed develops and to produce enzymes that can be used by the growing seed.

At the *distal* end of the barley corn is the endosperm. This collection of cells contains the starch needed by the growing seed and by the brewer. Each cell in the endosperm is made up of walls that contain a significant amount of β-D-glucan (see Chap. 2). Inside those cells, surrounded by a protective layer of proteins are the granules of starch. Those proteins include the large hordein (~35 %) and glutelin (~30 %) storage proteins that are used in the production of amino acids during growth. Also included are the albumin (~5 %) and globulin (~30 %) proteins that are the source of the enzymes needed by the seed during growth.

Finally, the *pericarp*—a semipermeable membrane that surrounds the corn—and *testa*—a thinner membrane that contains much of the compounds that result in the haze found in beer—are fused together to form the outer protective layers. Just outside of these layers is the *husk*. The husk is a collection of dead cells that contain a significant amount of silica. It is for this reason that the husk is both abrasive and hard. Along the dorsal side of the corn, the husk is known as the *palea*. The husk along the ventral side of the corn is known as the *lemma*.

Just inside the pericarp-testa lies the *aleurone* layer of cells as shown in Fig. 5.2. When the aleurone layer hydrates, it produces enzymes that help the seed utilize the endosperm's starches as food during growth. At proximal end of the corn, the husk

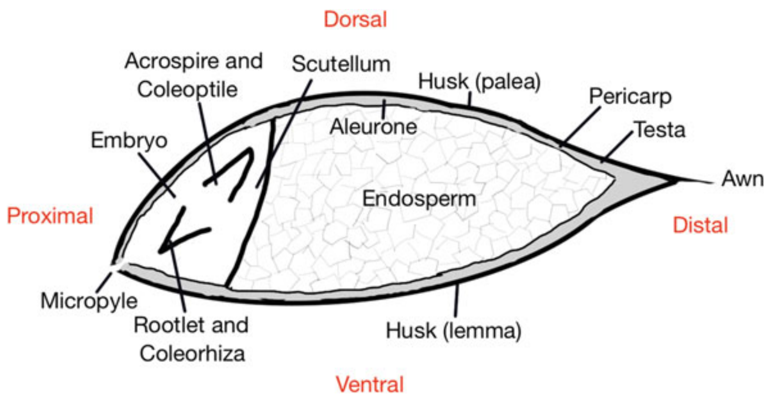

Fig. 5.1 Barley seed

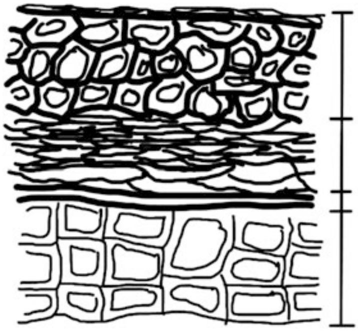

Fig. 5.2 A cutaway of the layers that make up the barley walls

has a *micropylar* region that is permeable to water. Because the aleurone layer is a little more permeable than the starchy endosperm, water that has entered the seed can travel along the outside edges of the seed.

CHECKPOINT 5.1
Describe the differences between two-row and six-row barley.
What is the difference between the coleoptile and the acrospire?

5.1.2 Barley and the Farmer

Barley has been grown nearly everywhere, however, it prefers cooler, drier climates. As a relatively drought-resistant crop, it can be planted either as a winter crop (planted in the Fall) or as a spring crop (planted in early Spring). The winter crop is harvested in July, the spring variety is harvested in August. Based on where the farmer lives, it may be possible to plant two crops in one year.

The world's largest producer of barley is Russia, followed by Germany, France, and Canada. Over 155 million metric tons of barley were produced worldwide in 2008. After a dip in production in 2010, the level of production has risen back to its current level of about 145 million metric tons. The USA is a relatively minor producer of barley. In 2015, the USA produced only 4.7 million metric tons of barley. This level of production is only 67 % of what was produced in the USA in 2000. The downward trend in barley production is due in some part to increasing prices for corn. In the current economy in the USA, as corn prices fall, so do the prices for barley.

Approximately 75 % of the barley used in beer production is grown in only five states in the USA; Idaho, Minnesota, Montana, North Dakota, and Washington. The remainder of the barley grown in the USA is distributed across a large number of states, primarily Utah, Colorado, South Dakota, Wisconsin, Wyoming, Oregon, and California. The influx of craft maltsters and microbreweries across many other states has driven some of the production of this valuable crop.

The farmer typically harvests when the moisture level in the seed is below 18 %. The barley is usually ready for harvest when it has less than 25–30 % moisture, but if it were threshed with this level of moisture, it would severely damage the seeds. So, the barley is either dried in the field or in the dryer attached to the silo until it is 12 % moisture.

Drying the barley after harvest occurs by either a batch dryer or a continuous dryer. One such batch dryer is known as the tower dryer. In this device, a large quantity of wet barley is conveyed onto a screen and then warm air applied. The air temperature is controlled to be about 40–50 °C (105–122 °F) as it passes through the grain. It is very important to monitor the temperature of the “air on”—the air that is passed into the grain—and the “air off”—the air coming out of the grain. This is done to make sure that the temperature of the grain itself does not rise above the 35–40 °C (95–105 °F) range. If it were allowed to get that hot, it could severely damage the barley corns. While the temperature of the air is much warmer than this, the evaporation of water from the corns helps to keep them cool. After a given amount of time on the screen, the barley is conveyed down to the next screen below and the process repeated. The series of screens are arranged in a tower pattern so that the air on at the bottom of the tower passes through multiple screens before exiting the tower. This type of dryer is relatively expensive, but efficient in drying the grain without damaging it.

An alternative to simply dropping the grain through the stream of warm air is the continuous dryer. Many different designs exist, but are essentially a long vertical tube where the grain is fed into the top and air blows horizontally across the grain. The dry grain is removed from the bottom of the tube. Improvements to this device have been made. One such improvement is a slanted conveyor (see Fig. 5.3). Grain is added to the conveyor and dried by blowing warm air through the conveyor. The air on is kept in the 55–60 °C (130–140 °F) range, and as the grain passes through the device, the air off tends to stay around 25 °C (77 °F). The grain is cycled through the drier until it reaches the 12 % moisture level and can be stored, although one pass is likely all that is needed.

In fact, barley must be stored before use. This allows the barley to “break dormancy”. Barley seeds, just like most seeds that are harvested, must be dried to about 12 % moisture and stored at around 35–40 °C (95–105 °F) to help break the dormancy before they can germinate and grow. If the freshly harvested barley seeds were planted without this resting stage, they would not grow. But after a few days at elevated temperature (depending upon the variety of barley), the seeds do sprout and grow when planted. And if not used immediately, they can be stored cool until they are needed.

There are many different cultivars of the barley plant that are used for making beer. And, there are a large number that are specifically used for feed. The American Malting Barley Association is one such source for a list of the different

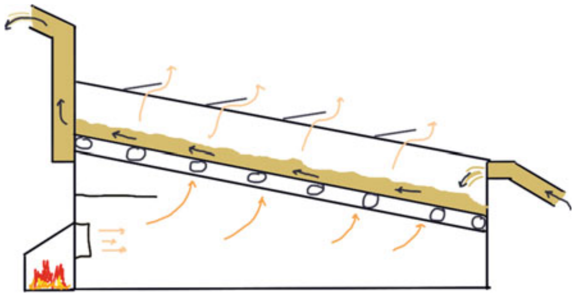

Fig. 5.3 Continuous barley dryer and air monitoring. The *orange arrows* indicate the flow of hot air (air on from the firebox, air off out the top of the device). The *black arrows* indicate the flow of the barley into the dryer and along the conveyor to the auger at the end of the device

cultivars. This organization makes recommendations to the farmers as to which cultivar of barley is likely to better grow and sell well in the coming year. They also track which cultivars were actually used and how many acres are planted in each.

5.1.3 Barley Diseases and Pests

Most farmers also have to worry about diseases and pests in their barley fields. In addition to reducing the yield of barley per acre, diseases and pests can cause damage to the product they make that can significantly reduce the price they get. The farmer knows these pitfalls very well and spends time watching for them. After all, good beer can be made from good ingredients. It is hard to make good beer from inferior ingredients.

The pests that inhabit barley in the USA are very damaging to the crops. One of the more common of these pests are aphids. There are a large number of species of these small insects, each causing its own specific damage to the barley plant. In addition to eating portions of the plant, aphids tend to cause the spread of sooty mold that can further injure the plants.

In addition to aphids, armyworms and wireworms can cause significant damage to the barley in the field. Wireworms tend to eat the young plants as they first grow. Armyworms feed on the leaves of the plant stunting its growth. The damage is not only noticeable, but treatable with pesticides and other pest-management practices.

Fungi can also cause damage to the crops and to the finished beer made from infected barley. One of the most notorious fungal infections is caused by the genus *Fusarium*. These fungi can result in “common root rot” that stunts plant growth or Fusarium Head Blight (FHB) that makes the seeds of the barley plant look like they are dried out. The fungus responsible for FHB, *Fusarium graminearum*, also produces a mycotoxin in addition to causing damage to the development of the barley plant. *Fusarium graminearum* releases deoxynivalenol (DON; also known by its common name: vomitoxin). This toxin is well regulated in the food supply with maximum levels set at 1 ppm. However, many farmers, maltsters, and brewers set even lower levels of this toxin.

Bread and beer made from grains containing DON cause nausea and in some cases vomiting, hence the common name for this compound. In addition, when barley infected with this compound is used to make beer, the mycotoxin forms crystals at the bottom of the bottles after bottling. If the level of DON is great enough, the crystals can get large enough to cause issues. When those bottles are opened a significant amount of gushing occurs, due to the sharp crystals of DON that provide nucleation sites for the formation of bubbles.

CHECKPOINT 5.2

Given that barley has a density of 609 kg/m^3, determine the pressure exerted on the bottom of a barley storage vessel that is 10 m tall and full of grain.

What would be the difference in the mass of 100 kg of barley that has 12 % moisture versus the same number of barley corns that have 18 % moisture?

5.1.4 Sorting and Grading

The brewer only wants the plumpest, most uniform, barley corns that they can obtain. And the farmers do their best to grow those. The maltster is the intermediary in this process. They are the ones that purchase the grain from the farmer, convert it into malt, and then sell it to the brewer. But they only buy those barley corns that are appropriate for the brewer, and they only pay the premium price when the barley corns are perfect and plump and free of debris.

So, the barley from the field is graded and sorted before being sold. The barley is first passed along a screen containing air jets and magnets. The air jets whisk away any light debris that might be present from the barley harvest. The magnets pick up any metal pieces. Metal shavings from the farm equipment, combines, augers, and other equipment can end up in the barley harvest. The magnet is needed to remove these shards. The screens on which the grain is moved allow miniature particles to fall through. These are typically small stones and other items that should be removed.

The barley then moves into a cleaning drum (Fig. 5.4). The drum contains a number of miniature scoops oriented around the inside. The drum is slowly rotated, and any small barley corns, broken corns, or other foreign material is picked up by the miniature scoops. This material, known as *dockage*, is damaging to the malting process. As the drum rotates the broken material moves along the perimeter of the

Fig. 5.4 Cleaning Drum. The drum rotates and carries dockage upwards. It drops in the center chute that conveys it out of the barley

barrel until it reaches the top. It then falls from the scoop and lands in a tube that runs out of the barrel. In this way, the barley is cleaned so that only corns remain.

In the final step, the barley is sorted into different grades. This step is very important to ensure that the barley used in the brewing process (or at least at the malting stage) is of the same size. Barley corns of the same size are needed because they will germinate at the same rate. If they are not graded, the final malt that the brewer receives will be of varying stages of modification (see Sect. 5.2), which will result in an uneven mash, and more importantly, an unpredictable result of mashing.

Grading takes place when a sample of the barley is placed in a hopper and then let out into a set of vibrating screens (Fig. 5.5). The top screen holes are 2.78 mm (0.109 in, 7/64″), the second screen is 2.38 mm (0.09375 in, 6/64″), and the third screen is 1.98 mm (0.078 in, 5/64″). Kernels that stay behind on the first and second screens are considered plump. Barley corns that pass through the second screen, but stay on top of the third screen are considered "thins". The kernels that fall through the third screen are considered "thru" or dockage.

Malting barley in the USA is graded based on the standards set by the USDA (United States Department of Agriculture). There are four grades available for malting barley based on the type of barley (six-row versus two-row) and on the

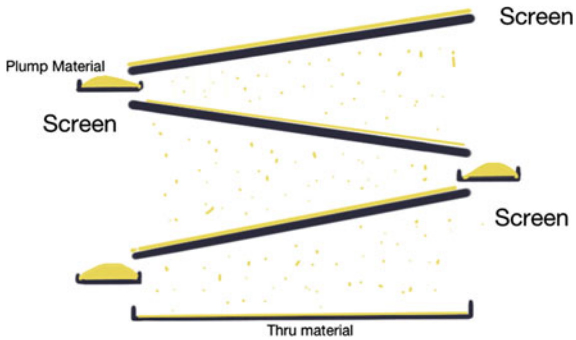

Fig. 5.5 Grading screens. The vibrating screens are held at an angle

Table 5.1 Maximum percent of thins allowed in the US graded malting barley

USDA Grade	Type	Maximum thins (%)	Minimum unbroken kernels (%)
1	Six-row	7.0	97
2	Six-row	10.0	94
3	Six-row	15.0	90
4	Six-row	15.0	87
1	Two-row	5.0	98
2	Two-row	7.0	98
3	Two-row	10.0	96
4	Two-row	10.0	93

amount of plump, thins, and thru. Table 5.1 lists the maximum amount of thins that can exist in any of the grades.

The percentage of plump kernels in any grade can be requested in an analysis of the grain sample. The higher percentage of plump kernels is highly desired in a quality malt sample, irrespective of the USDA Grade. From Table 5.1, the maximum percent thins indicates that the best Grades (1 and 2) require more than 90 % plump kernels. Samples that do not conform to these standards are typically graded in the “barley” category and are used as food or feed.

5.2 Malting Barley

Once the barley arrives at the maltster, the workers use the natural machinery of the barley itself to convert it into malt. There are three main processes involved in malting the barley. These are steeping, germination, and kilning. We will explore each of these processes from both the aspects of what goes on inside the barley corn and what equipment accompanies each of these processes.

5.2.1 Germination of Barley

In the malthouse, the incoming barley is steeped in water. It is very important that the water be high quality because it will be absorbed by the barley and carried forward into the finished beer much later in the process. When barley is soaked in water, some of the water enters the seed through the micropylar region. The water then hydrates the embryo and the aleurone. The influx of water causes the activation of the biological machinery inside. The husk also begins to absorb water, passing it into the pericarp and testa by capillary action (Fig. 5.6).

The water moves slowly through the barley seed from the proximal to the distal end and much faster along the dorsal edge. The vascular structure of the seed along the dorsal side means that water moves by capillary action faster. The seed becomes

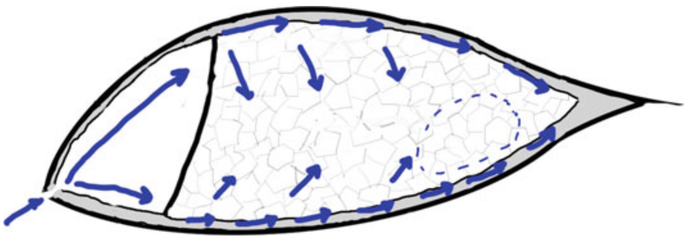

Fig. 5.6 Water movement as a barley seed hydrates. The *dotted blue circle* is the last place to become hydrated

hydrated from the embryo through the scutellum and into the aleurone layer. Then the endosperm becomes hydrated from the outer edges toward the center. The movement of water is fairly slow through the endosperm, such that the entire seed is only fully hydrated when it is soaked in water.

The goal for the maltster is to make sure the barley increases to about 45 % moisture. Too little moisture and it will not germinate fully. Too much moisture and it will rush too quickly through germination. Neither of these two options is useful for the maltster. Typically, it takes between 30 and 50 h to reach this level of moisture.

Once hydration begins, the embryo and scutellum begin to produce *gibberellic acid*. Gibberellic acid is a plant hormone, and just like human hormones, it triggers other actions inside the seed. Specifically inside the barley seed, it diffuses into the aleurone layer and signals the production of enzymes needed by the seed to grow (Fig. 5.7). Because of the way the seed hydrates, the gibberellic acid moves to the dorsal side of the seed and then moves to the distal end. Enzymes are produced wherever it goes, and the pattern of their production means that the seed “grows” in an asymmetric pattern. The last portion of the seed to be affected by the enzymes is located near the distal end on the ventral side (it is the same location as the last place that gets hydrated).

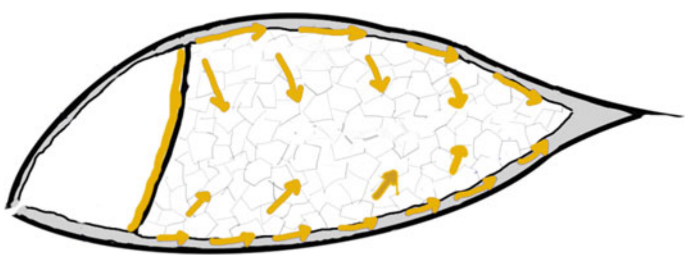

Fig. 5.7 Activation of enzymes by gibberellic acid. Gibberellic acid (represented by the *orange color*) is made in the scutellum and passed into the aleurone layer. From there it migrates through the aleurone activating enzymes. Those enzymes then diffuse into the endosperm

The enzymes that are activated include those that are already produced by the seed and are awaiting hydration. These are known as zymogens and only require water to become active. Gibberellic acid also signals the biological machinery in the aleurone layer to make enzymes from scratch as well. The enzymes generated by the growing barley seed include:

- α-amylase—converts starches into useable sugars
- β-amylase—converts starches into useable sugars
- limit dextrinase—breaks starches into smaller pieces
- glucanase—breaks down the cell walls in the endosperm
- pentosanase—breaks down the cell walls in the endosperm
- protease—breaks down the proteins that make up the cell walls and surround the starch granules in the endosperm
- phytase—releases phosphate from phytin and lowers the pH

Each of these enzymes is covered in greater detail in the chapter on mashing. However, as we can tell from the listed actions that each performs, the main goal of the production and release of these enzymes is the conversion of the starches in the endosperm into sugars and the proteins into amino acids. This soup of nutrients is then taken up by the scutellum and given to the growing embryo.

The degree to which the endosperm is *modified* by the action of water and enzymes is very important. If only a portion of the endosperm is modified, the resulting malt is considered *partially modified*. If all of the endosperm is modified, the malt is considered *fully modified*. Fully modified malt is squishy and spongy to the touch—a good indicator that the endosperm's cell walls have been broken down. Partially modified malt contains a hard nib inside the malt that is not broken down by the enzymes. This becomes very important in mashing as the fully modified malt can be easily converted into fermentable sugars. The partially modified malt must undergo additional processing during the mash in order to be completely converted into fermentable sugars.

More importantly, partially modified endosperms have a significantly larger amount of β-glucan remaining. This carbohydrate that makes up a portion of the endosperm cell walls causes some problems for the brewer unless it is taken care of during malting. Of primary concern is that it makes the grain bed during mashing much less permeable, a problem that can give rise to a stuck mash. In addition, the large amount of β-glucan in the mash can translate into haze in the finished beer.

The proteins that make up the cell walls and surround the starch granules are broken down into amino acids by proteases. This contributes the amount of free amino nitrogen (FAN) available in the grain. FAN is useful for the fermentation process because the yeast need these small amino acids and amines as nutrients. Some proteins are only released and not completely degraded into amino acids. Four different protein classes have been identified: albumins, globulins, glutelins, and hordeins. The albumins and globulins are smaller proteins that tend to be more water soluble than the glutelins and hordeins.

High levels of protease activity initially seem like they would be a good thing to have happen because higher levels of FAN would be beneficial to the yeast later in the process. However, this is not the case. If the level of FAN is too great, the amount of Maillard reactions (the heat driven reactions of amino acids and sugars) increases. This can result in significantly more browning and caramelization than desired. In addition, if too many of the proteins are broken down, the result is a loss of the head on the beer. The combination of proteins, tannins, and other compounds is needed to support a full head of foam.

If the level of protease action is too low, many of the proteins will not break down. This results in problems with haze and foam later in the process. It also results in a lower than usual conversion of the starches into fermentable sugars during the mash. High protein levels can result in a more viscous wort during mashing, increasing the risk of a potentially stuck mash. Finally, the foam generated during the initial stages of the boil can be quite significant meaning additional care must be taken prior to the hot break. In short, it is very important to have adequate protein degradation.

The end result of all of these steps is the growth of the barley seed. Initially, the maltster notes the emergence of the *chit* from the bottom of the seed. This will eventually develop into the roots as the seed continues to grow. The maltster also notes the growth of the acrospire that eventually will become the shoot for the plant. The acrospire grows from the embryo under the dorsal husk of the seed toward the distal end. Basically, it is not seen during the initial stages of growth—but if a seed is pulled apart, the acrospire can be readily observed.

The maltster stops the growth of the seed as soon as the acrospire is approximately the same length as the entire seed. By this time, the roots are about two-times the length of the seed. This amount of growth is required for the endosperm to become fully modified. If stopped too early, the malt would be partially modified. If the maltster does not arrest the growth of the seed when the acrospire is as long as the seed, the level of starch in the endosperm would continue to drop as the seed grows and the utility of the seed to be used in making beer would be reduced.

To stop the growth, the maltster applies heat and dries out the seeds slowly until they are almost free of moisture. The dehydrated seed cannot continue growth and the enzymes are unable to continue to act on the starch and cell walls. The enzymes are, for the most part, still active. They just lack the water to allow them to do their work. At this point, the malt can be kilned to add color or flavor to the malt itself.

5.2.2 Equipment Used in Malting

In the previous section, we uncovered what happens inside the barley seed as it undergoes the malting process. The maltster uses some specialized equipment to ensure that the process is efficient, rapid, and uniform across an entire batch of barley. Special attention is placed on making the process uniform. Deviations from uniformity result in partially, fully, and over modified malt. Such malts would be difficult to handle in the brewhouse and would lower the mash efficiency for the brewer.

The first step in the process after cleaning, sorting, and grading the barley is to steep it in a vessel. This can simply involve soaking the barley in a vat for a period of time. To ensure that the barley does not "drown", oxygen bubbles through the mixture. The action of the gas in the vat helps to stir the mixture. Unfortunately, this leaves areas in the vat that have significantly more oxygen exposure than other areas. The stirring action of bubbling gas tends not to mix very efficiently either.

So, the maltster has developed a more efficient steeping tank. This tank looks very similar to the cylindroconical vessels (CCVs) that are used as fermentation tanks. However, the interior of these vessels belies their difference. Figure 5.8 illustrates a drawing of a cutaway view of the modern steep tank. The sloped bottom and internal baffles force the slurry of water and barley to mix thoroughly. This provides adequate water and oxygen uniformly to the barley seeds.

The steeping of the barley is adjusted by the maltster to allow even hydration. Often this includes periods of soaking in water, periods of bubbling oxygen through the water, and periods of resting (where the water is drained). It is very important that the soaking cycles include cycles of resting. Resting allows the removal of CO_2 and waste products from the barley as it grows. Resting also is important because it allows the barley to be washed of foreign substances and bacteria.

The barley seeds generate heat as they absorb water and swell in size. Initially, the maltster starts the steep by adding water that is between 15 and 20 °C (59–68 °F). The heat generated by the germination process can raise the temperature of the water as high as 25 °C (77 °F) before it is drained and refilled. This might not seem like a significant change that we would worry about, but it is. As the temperature increases, the speed of the germination increases and is less able to be controlled. Remember that the maltster is working hard to accurately control the entire process in order to make sure that every barley seed in the batch has the same modification. Higher temperatures make this harder to accomplish. More

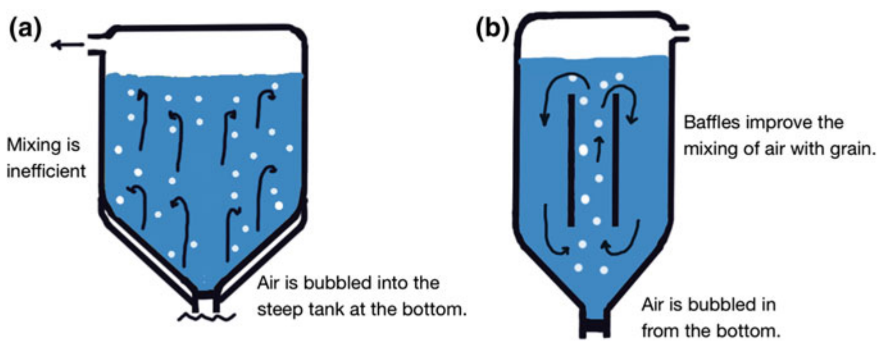

Fig. 5.8 Steep Tank designs. **a** Traditional design with poor uniformity. **b** Modern design with good mixing and uniformity

importantly, if left unchecked, the temperature could get high enough from the mass of barley to damage it during the germination step.

Once the water content in the barley seeds rises to about 45 %, the barley is moved to a vessel and allowed to sprout. There are many different types of germination vessels. Traditionally, the hydrated barley was spread out onto the floor of a building. This process, known as floor-malting, is still practiced. Some brewers and maltsters believe it provides a very uniform modification and a handcrafted taste to the malt. After spreading it out into a layer on the floor, the barley is turned over multiple times until the germination is complete. Turning can be accomplished by hand (where the maltster uses a hoe or fork to turn the barley) or by machine. Typically the entire germination process takes between three and five days.

Turning the grain as it germinates has the same effect as cooling the grain. Reduction of the heat is just as important during germination as it is during steeping. If left unchecked, the hot grain supports the growth of bacteria. In addition, as the grain gets hotter, it begins to become uneven in its rate of germination. Warmer seeds begin to *bolt*—germinate very quickly. And the entire germination process becomes uneven.

Other alternatives to floor-malting include drum-based malting systems. In the 1880s, Frenchman Nicholas Galland developed a drum to germinate barley (Fig. 5.9). Its use in malting barley was an immediate success. The Galland Drum is essentially a large drum with perforated tubes that run down the inside of the drum's perimeter. The axis of the drum is also a perforated pipe. Air is blown into the tubes along the perimeter and exits through the center pipe. Periodically, the drum rotates to turn the grain.

Charles Saladin, a French contemporary of Galland, invented a germinating vessel that bears his name. First introduced in the 1890s, the Saladin Box (see Fig. 5.10) is a rectangular cement box with a false perforated bottom for air flow. Modern versions of the Saladin Box are round instead of rectangular. The addition of a rotating arm to the top of the round box allows the grain to be evenly added to the germinator. Steeped grain is placed into the box to a depth of 0.9–1.2 m (3–4 feet). Along one end of the box is the air intake. The intake also includes

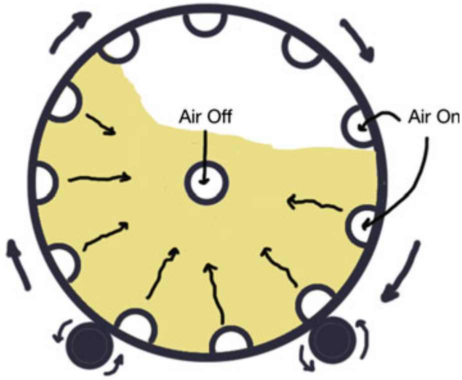

Fig. 5.9 Galland Drum. Air enters through the tubes along the perimeter and exits through the central tube

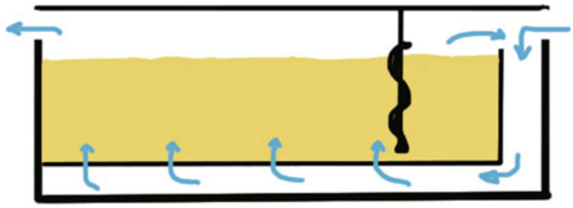

Fig. 5.10 Saladin Box. Air, represented with the *blue arrows*, can be recycled and the humidity and temperature adjusted. The screws move along the length of the grain bed turning it over gently

humidifiers to keep the air moist and prevent the growing seeds from drying out. Air is passed into the intake and up through the false bottom. It exits the top of the box. In some systems the entire box can be covered so that the exiting air can be recycled. At the top of the box is an arm containing large screws that rotate and move along the length of the box. The screws gently turn the growing grain.

The Wanderhaufen was a germinating system invented by the founder of the Carlsberg brewery in 1878 (Fig. 5.11). Steeped grain is placed at one end of the device at a shorter depth than in the Saladin Box and fully modified malt exits at the other end. The grain rests on a perforated false bottom, and in a manner similar to the Saladin Box, air is pushed through the bed of grain. Slanted turners move the grain from one portion of the device to the next. This movement turns the barley as it grows. By the time the barley has reached the end of the device, it is fully modified.

As the grain germinates, controlling the temperature of the grain becomes more difficult. For this reason, the maltster allows the grain to dry out a little in a process known as *withering*. The control of germination can also be accomplished by increasing the amount of CO_2 that is added to the air passing through the grain. This slows the respiration of the grain and reduces its growth rate. A slower growth rate allows the maltster to more carefully gauge when it is finished.

Once the grain has reached the modification level desired by the maltster, it is known as *green malt* and is pumped into the *kiln*. This sounds like a very hot oven, but just the opposite is true. The kiln is instead a process by which warm air is passed through the malt until the malt's moisture content is reduced to about 4 %. The green malt is pumped into a vessel with a perforated false bottom. Air is blown under the false bottom and up through the malt bed.

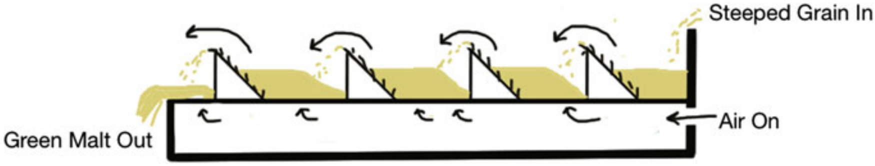

Fig. 5.11 Wanderhaufen. The air enters under the false bottom and blows up through the germinating grain. Slanted turners move the grain along the device. Unlike the Saladin Box and other germinators, this system allows continuous germinating of the grain

The effects of kilning reduce the moisture in the malt and inhibit the further growth of the barley seed. Control of the removal of moisture is very important, just as is every other step in the malting process. That control comes about in the kiln and how it operates. If the malt is dried and kept cool, most of the enzymes that are in the seed will remain “alive”. Just as in the dry barley seed though, they will nott have any water present, and so will not be active. The kilning process involves the following steps:

1. Free Drying
2. Forced Drying
3. Curing.

In the *free drying* step, warm air (50–60 °C, 120–140 °F) passes through the grain with a high flow rate. The moisture in the seeds slowly evaporates and is removed from the malt. Because evaporating water requires energy, the malt is cooled as the moisture content drops. This initial stage takes about 12 h and results in the reduction of the moisture content of the malt to about 25 %.

The maltster pays attention to the humidity of the air off. It is very desirable for the air off to have 90–95 % humidity. However, if the humidity reaches 100 %, the moisture in the air might condense on the kiln itself. This causes a severe problem with the malt. Since the air cannot support additional water (i.e., humidity) the air on slowly cooks the malt. This not only increases the color and flavor of the malt (see Sect. 5.3), but also destroys the enzymes inside. This detrimental effect is known as *stewing*.

Once the free drying is complete, the malt enters the *forced drying* stage. This stage occurs when the air off humidity levels start to decline and the temperature of the air off rapidly begins to rise. This point is known as *breakthrough*. The decline in humidity indicates that the moisture in the outer part of the malt has evaporated. What remains is the water deep inside the malt. Getting this out requires higher temperatures (about 70 °C, 158 °F). The process does not take long, but eventually the moisture in the malt has dropped to about 10 %. Because the amount of moisture in the malt is significantly reduced, there is little cooling effect during this stage. The result is that the temperature of the air off begins to rise.

Once the air off and air on get close to each other, the malt enters the *curing* stage. In this stage, the temperature of the air on is increased to about 85 °C (185 °F) for lager malts and to about 100 °C (212 °F) for ale malts. In this stage, the moisture content is reduced to about 4 %. The curing stage only lasts about 2–3 h. Figure 5.12 illustrates the temperatures of the air on, air off, and moisture level of the malt during kilning.

As soon as the malt is cured, the temperature of the air on is dropped quickly to cool the malt. At the end of the entire process, the malt is stored cool to allow the remaining moisture in the seed to redistribute evenly across the seed. Storage times of up to a month may be required for certain malt cultivars.

Kilning actually requires a significant amount of energy, as the air on must be constantly heated. Traditionally, the energy has been provided through the burning

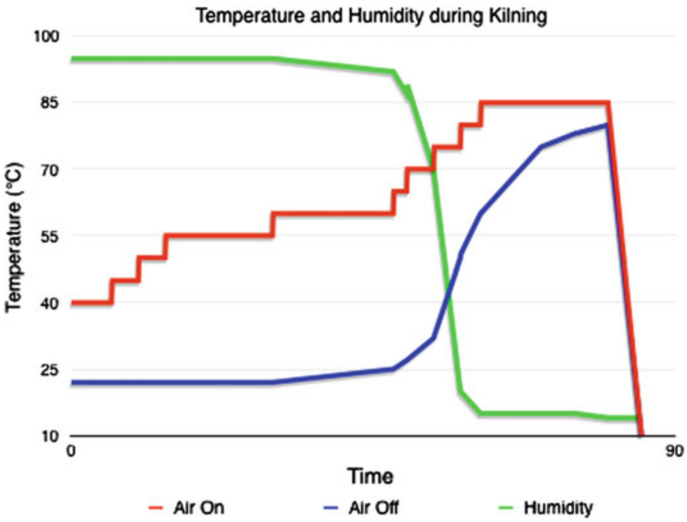

Fig. 5.12 Kilning temperatures. The red line is the air on, blue is the air off, and green is the moisture content of the malt itself

of wood, coal, or fossil fuels (such as natural gas). The heat from the burning material was passed directly through the false bottom of the kiln. Modern kilns heat water that passes through a radiator. The air on is fed through the radiator to be warmed and then through the malt. This reduces the flavor impact of burning wood, coal, or fossil fuels on the malt.

Given the cost of construction, many malting plants (aka *maltings*) are designed in a tower format. Barley is conveyed to the top of a multi-story building. There it enters the steeping process. Upon completion of steeping, the grain is conveyed to the next floor down and enters the germination process. It may be moved additional floors and go through additional germination steps. Finally, it enters the kiln in the bottom floors. In this way, the amount of land required to operate a maltings is reduced. The entire facility is known as a *tower maltings*.

Once kilned and dried, the malt may be further kilned at elevated temperatures to provide malt with more color and flavor. Simply kilning at an elevated temperature gives that result. In other cases, the malt is quickly re-steeped and then placed back in the kiln. The air on is re-humidified to 95–100 % and the temperature increased to 66 °C (150 °F). This causes the malt to begin to mash (see Chap. 6) and the sugars begin to form. After an hour, the humidity is reduced and the malt kilned until dried back to about 4 %. This results in crystal or caramel malt.

5.2.3 Problems Arising from Malting

Malting barley requires the use of hot air. The traditional method of applying heat directly to the air on through the use of burners causes the production of NO_x. NO_x

is a general formula for a series of compounds that include NO and NO_2. These compounds are gases that when exposed to the germinating barley can react with amines (such as those found in amino acids and proteins) to form nitrosamines. Of particularly notorious reputation is N,N-dimethylnitrosamine (NDMA), a carcinogen that is highly regulated. For example, the World Health Organization limits NDMA in drinking water to no more than 0.1 parts per billion. The use of indirect heating of the air on, use of the lowest temperatures possible to accomplish the malt drying, and increased air on flow rates have significantly reduced this issue.

In germinating malt, the amino acid methionine undergoes a reaction to form S-methylmethionine (SMM). When the malt is kilned, the heat causes the decomposition of SMM into dimethylsulfide (DMS). The warm air on drives off most of the DMS, but a small amount becomes oxidized into dimethylsulfoxide (DMSO). DMSO is less volatile and can remain in relatively large amounts in the finished malt. Increased heating reduces both DMS and DMSO during the kilning process, but this comes at the expense of darker malt with increased Maillard reactions.

DMS imparts a creamed corn or canned corn flavor to the malt. Unless this is removed or reduced significantly, this flavor will be found in the finished beer. While this flavor may be desired in some beer styles such as the Pilsner style, it is not desirable in many. DMSO has a garlic-like flavor that is not desirable in most beer styles.

CHECKPOINT 5.3

Smoked malts are usually kilned over a wood fire. In addition to the flavor of the smoke, what would you predict would also exist in the malt?

Describe the differences between fully modified and partially modified malt.

5.3 Maillard Reactions

When heat is applied to the combination of sugars and amino acids, the result is their combination and reaction to form flavor and color compounds. The reaction, described in Chap. 2, is fairly complex, but the amounts of flavor and color are directly related to the time and temperature of the system.

The first step in the reaction sequence involves the condensation of an amino acid and a reducing sugar as illustrated in Fig. 5.13. The reducing sugars that exist in malt are the same as what exist in wort and include glucose, maltose, maltotriose, etc. In malt, these compounds are not as prevalent as those in wort, but exist in quantities sufficient enough to result in the browning and flavor that we attribute to kilned malts. The amino acids that exist are the result of the action of the proteases on the starchy endosperm.

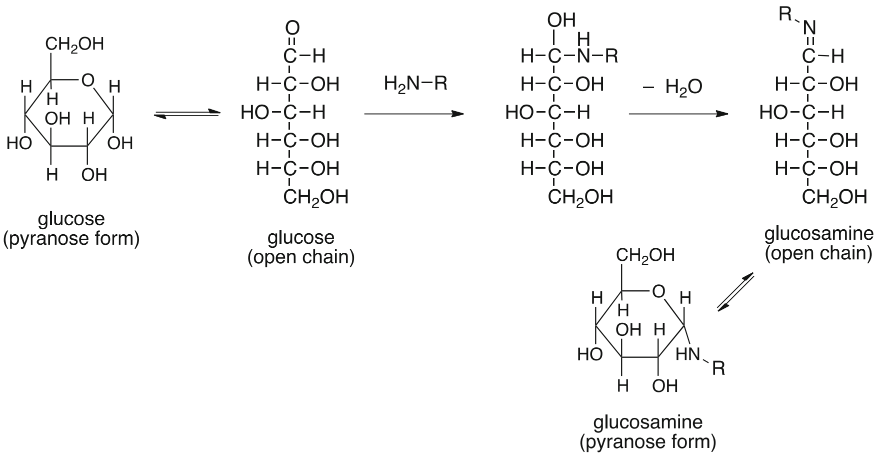

Fig. 5.13 First step in the Maillard Reaction. The amine group (H2 N–) is a part of a larger molecule, such as an amino acid, protein, or other compound. The “*R*” stands for the rest of the molecule to which it is attached

While Fig. 5.13 illustrates the reaction with glucose, the action of maltose with amino acids produces a similar compound. This first reaction is catalyzed by heat. The initial addition of the amine functional group of an amino acid or protein to the carbohydrate is relatively unstable and eliminates water to give rise to glucosamine (or maltosamine, or etc.). Glucosamine and maltosamine can then re-cyclize into the pyranose form that is relatively stable.

The second step of the reaction is illustrated in Fig. 5.14. This step, named after the Italian chemist Mario Amadori, is known as the Amadori Rearrangement. This reaction is proposed to be acid and heat catalyzed. It involves reopening of the ring and then rearrangement of the double bond to the more stable carbonyl (C=O). This compound, an aminoketose, can also re-cyclize into the pyranose form.

It is at this stage that the Maillard Reaction can go one of three ways. In the first pathway (Fig. 5.15), the aminoketose can dehydrate and lose a single water molecule. That results in dicarbonyl compounds, many of which require a rearrangement to more stable compounds. The products of this first pathway are very similar to the products of caramelization (the reaction of carbohydrates with heat). Words used to describe the flavors of these compounds are caramel, toffee, and sugary.

The second pathway (Fig. 5.16) involves the extensive dehydration of the aminoketose. The product of the initial dehydration then undergoes the Strecker degradation (named after German chemist Adolf Strecker who discovered it in the 1860s). The product of the Strecker degradation is an aldehyde (known as the Strecker aldehyde) and an aminoketone. These products alone have nutty, buttery,

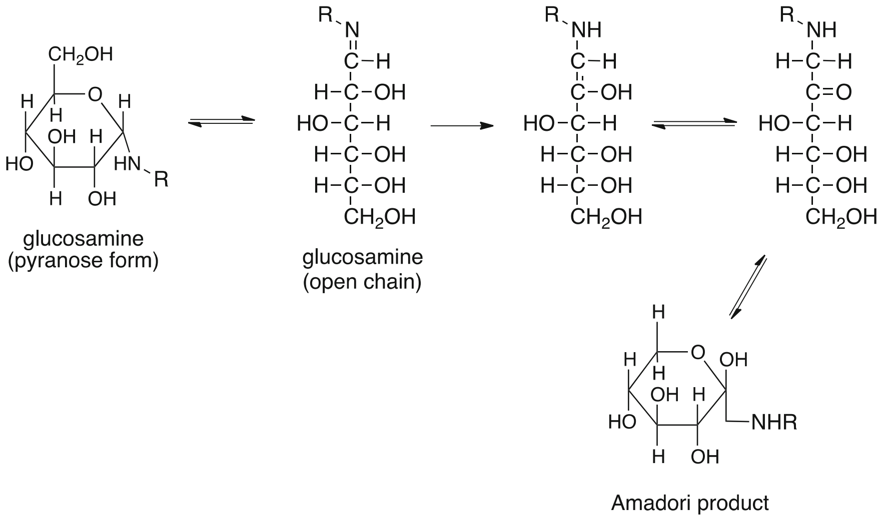

Fig. 5.14 Second step in the Maillard Reaction—the Amadori Rearrangement

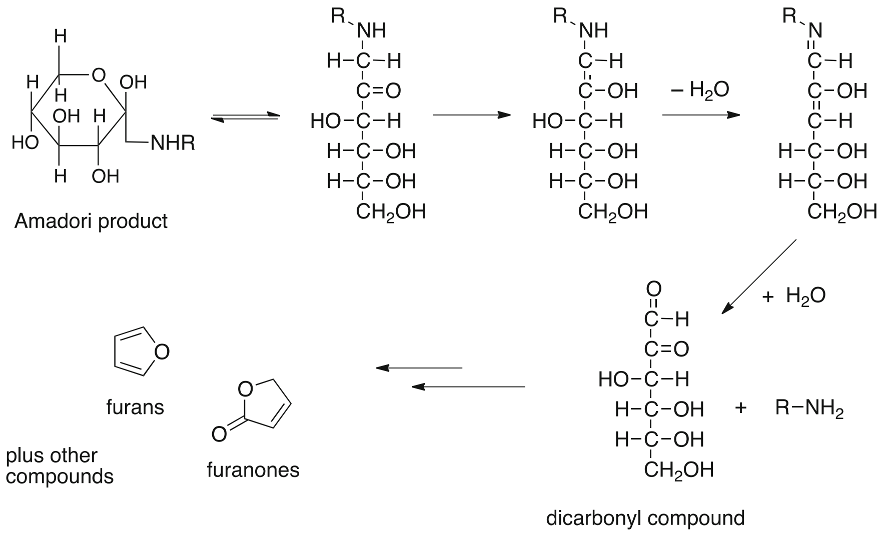

Fig. 5.15 Dehydration gives rise to dicarbonyls that can make compounds with caramel flavors

or butterscotch flavors and can contribute to the aroma of the malt. Further reaction of these compounds gives rise to cyclic compounds such as maltol and isomaltol. In fact, kilning of Munich malt imparts a malty flavor to the finished beer. That flavor is the result of relatively large amounts of maltol and isomaltol.

The third pathway gives rise to the melanoidins. Extensive heating or high temperatures form these compounds. Melanoidins are very complex and arise from multiple dehydrations and then combinations of other amino acids, carbohydrates,

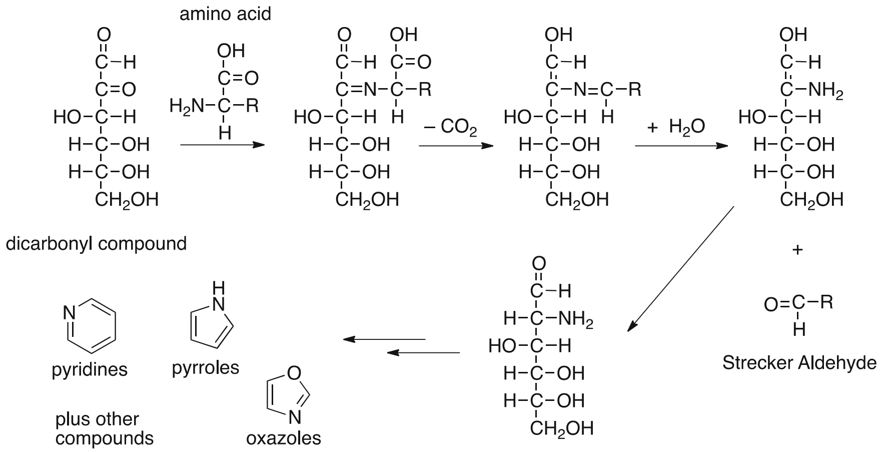

Fig. 5.16 Strecker degradation and related products. The amino-carbonyl product of the Strecker Degradation can make compounds with burnt, astringent, toasty, and nutty flavors

or compounds from any of the other steps in the Maillard Reaction. In other words, these compounds are not well characterized. However, the large polymeric structures are highly colored and can have an astringent, bitter, burnt, or roasty flavor.

CHECKPOINT 5.4

Given the structure of glucosamine that results from the reaction of an amino acid with glucose, draw the structure of the product of the same amino acid with maltose.

Can malt or other compounds containing sugars and amino acids under Maillard reactions occur at room temperature?

5.4 Water—The Most Important Ingredient

Water is the most important ingredient in the production of beer. As we noted in this chapter, the use of steep water requires that the water is purified or treated. The same is true for the next steps in the brewing process. The properties of mash water, also known as hot liquor, can significantly impact the quality of the finished beer.

In this section, we will uncover this ingredient, discover where it comes from, and explore the different compounds and ions that can be present in water. Knowing this information will help us understand how this ingredient can result in changes to the flavor and processes involved in making beer. Let us start by looking at where this valuable resource comes from.

5.4.1 Types of Water

There are three main sources of water available to the brewer depending upon where the brewery exists. These sources include rainwater, surface water, and groundwater. The hydrologic cycle, the description of how water moves through our environment, describes the interchange of these sources of water. Initially, surface water evaporates and forms clouds. Clouds are primarily made up of water, but due to their exposure to the gases of the atmosphere can have some of these gases dissolved in the droplets of water. The gases found in clouds include carbon dioxide, methane, sulfur dioxide (from volcanoes and the burning of fossil fuels), and NO_x (from forest fires and the burning of fossil fuels). Clouds that form over oceans and other salty waters can also contain very small amounts of ions such as sodium, chloride, and potassium.

Clouds can traverse many miles from where they are formed before precipitating as rain or snow. And since the rain comes directly from the cloud, the rain and snow contain the same dissolved gases and ions as were found in the clouds. Due to the compounds dissolved in the rain water, the pH tends to be around 5.5. In the not too distant past, when the regulations on industrial emissions were much more lax than they currently are, the pH of rain was routinely in the 2.0–4.0 range. In fact, the lowest recorded pH of rain occurred in West Virginia in 1978. That rain had a pH just under 2.0. As a point of reference, stomach acid has a pH of 2.0.

Once on the ground, the rain and snow melt into streams, rivers, and eventually end up in lakes and oceans. Water on the surface of the earth comes into contact with plants, soil, rocks, and pollutants from human and other sources. Prolonged exposure to rocks and soils is required for any significant quantities of ions to be present. However, the acidity of the rain can greatly reduce the time required for the water to "pick up" dissolved ions such as calcium. Plants and animals can also greatly impact what is dissolved in the water. Tannins from decaying leaves, bacteria, algae, and other compounds from dead animals can be part of the stream of water. Coupled with the interaction of living creatures with the surface water, this organic material significantly changes the perceived and actual quality of the water.

There are two "spurs" on the hydrologic cycle. One results from the location where snow collects after it has fallen to the ground. Snow can fall in locations that rarely melt, such as at the poles or in glaciers. Ice and snow eventually do melt and are returned to the surface waters of the hydrologic cycle. The other spur results from the permeation of water into the ground. This water can flow just like streams and rivers and can re-enter the surface waters via springs. Often it takes years for the water to return to the surface.

Only one important reservoir occurs in the cycle. Storage of water outside of the hydrologic cycle can occur when the water permeates down into the soil into underground lakes that do not return to the surface at some other location. It can take hundreds of years for the water to enter these aquifers, providing significant time and pressure to dissolve ions from the surrounding rocks. Because the water must filter down through the soil and rocks, it is often less contaminated by the organic material found in surface waters.

5.4.1.1 Aquifers

There are more than 64 principle aquifers in the US alone, according to the United States Geological Service. Particulars on each of these aquifers can be found by visiting their Web site (water.usgs.gov); however, there are five basic types of rock that line these aquifers. Knowing these basic types will give us a good background on what we can expect from our water.

- Sand and gravel
- Sandstone
- Sandstone and carbonate
- Carbonate
- Igneous and metamorphic.

Sand and gravel deposits that line aquifers are permeable and recharge fairly quickly. Prior to the withdrawal of water via wells, most of the water in these aquifers was able to flow into adjacent aquifers or other groundwater sources (such as oceans or rivers). Because the water can flow readily within, into, and out of these aquifers, the water tends to have slightly higher quantities of organic material. Runoff from agriculture and industry can pollute the water fairly easily. In addition, the water within the aquifer can be relatively high in ions that characterize the location of the aquifer. For example, central California is home to a large sand and gravel aquifer. Water from this aquifer can contain relatively high levels of ions such as iron, sodium, boron, arsenic, and chloride. Many of these ions are the result of intrusion of seawater into the aquifer.

Sandstone lined aquifers have fairly small pores and fractures within the rock. As such, the beds are permeable, but flow of water is restricted to mostly local areas unless the fracturing is fairly extensive. In places where the fracturing is extensive, contamination of the water from agricultural or industrial sources is possible. The pores within the sandstone do a good job of filtering organic materials, but the fractures do not. The intimate contact of the water with the rocks means that the water tends to have fairly large concentrations of calcium, magnesium, and bicarbonate. And, because of the presence of fractures, the ground water can have up to intermediate levels of organic solids and other materials dissolved within it. Western Colorado contains an example of the sandstone aquifers. This particular aquifer has extensive fracturing as indicated by the intermediate level of organic material and high to very high levels of *hardness* (calcium and magnesium).

Carbonate aquifers often have large caves, pipes, and other openings within the rock in which the water rests. Flow of the water within the aquifer is relatively restricted, except in those areas where the caves and openings resulting from dissolving of the rocks are rather extensive. Contamination of the aquifer in these areas can be an issue because of the flow of the water. The amount of organic material in the aquifers is variable, also due to the presence of the openings along the rocks within the system. Calcium, magnesium, and bicarbonate tend to predominate the ions that are found in the water making the water hard to very hard. While other ions tend not to be an issue, sulfate concentrations can be higher in those regions where deposits of lead and zinc exist. For example, southern Missouri is home to a carbonate aquifer, and, as a visit to the area will confirm, there are a significant number of caves and freshwater springs in the area. The springs arise from the fact that the aquifer is very close to the surface of the ground in some areas. This allows the aquifer to discharge directly to the surface, become replenished easily with rainfall, and, unfortunately, be easily contaminated with agricultural and industrial runoff.

Sandstone—carbonate aquifers—contain a mixture of sandstone and carbonate rocks in which the aquifer lies. While pore size is fairly small, the movement of groundwater in these aquifers can be quite large. In fact, the most productive wells in the USA are located in the city of San Antonio, Texas, located on the Trinity-Edwards aquifer (an example of sandstone-carbonate aquifers). These wells can produce more than 16,000 gallons of water per minute. Organic solids tend to be low to intermediate in concentration. But, just like the individual sandstone and carbonate aquifers, the concentration of calcium, magnesium, bicarbonate, and carbonate ions tends to be fairly large. The concentrations tend to be high enough that the water is considered very hard and relatively basic ($pH > 7$) due to the carbonate and bicarbonate concentrations. Many of these aquifers tend to be located fairly close to the surface of the soil, so they are easily replenished from surface waters and contamination can exist.

Igneous rock aquifers are the least permeable of the aquifer types. These rock systems result from depositing molten rock onto the ground and then over time becoming buried in the ground. The result is a dense rock formation that is often crystalline or fused in nature. Water permeability, then, is limited to fractures within the rocks. Often, multiple layers of igneous rocks occur together, with fractures between the layers. Water moves through fissures in the layers and between the layers to fill the aquifer. The results are limited filtering of the water and few ions from dissolution of the surrounding rocks.

5.4.1.2 Brewery Water

For the brewer, there are three main places to get water. The first involves collect it as rain. This is actually illegal in some locations in the USA. Because the compounds that dissolve in rain are variable based on the makeup of the atmosphere at the time it rains, a problem exists in the use of this water. To accurately understand what is being used, the brewer must analyze each and every sample before its use in brewing. More importantly, unless the brewery is located in a rainforest, the quantity of rainwater is likely not sufficient to serve as the sole source of water for the brewery. Even pilot batches of 1–2 bbl would require significant quantities of water that could not be routinely supported in most areas of the country.

The second place the brewer can obtain water is from a well. Wells can be dug deep enough to reach into an aquifer, or may be shallow so that they depend solely on groundwater below the water table. While the aquifer option is likely the best, it may not be possible to dig that deep. So, some of the wells in use only dip into the ground water supply under the water table. Water quality of these shallow wells is better than the surface waters surrounding, but in some cases not much more.

For the deep wells that take water from the aquifer, the ions and species in the water are a result of the type of rock associated with the aquifer. For example, a brewery located in the southeastern Kansas region would be using water from carbonate rocks. The water would be very hard, with high levels of calcium and magnesium. The pH of the water would likely be at or above 7.0 due to the high levels of carbonate ions. The brewer would want to periodically test the water for contamination from agricultural sources and for organic materials as these could periodically become large enough to damage the flavor of the finished beer. While unusual, the brewer may also want to check for the presence of bacteria or other microorganisms indicating further contamination.

The third, and most common, place to obtain water for brewing comes from a municipal supply. In fact, most brewers will not have an option and be forced to use water supplied from their town. Across the USA, cities and towns get their water from surface and ground water supplies as needed. Some towns pull water from nearby lakes, some from rivers and streams, some dig wells, and others use reverse osmosis to grab water from oceans. In fact, larger towns and cities may obtain water from multiple sources. It all depends on where the closest water supply exists.

Thus, the water delivered to a brewery is highly dependent upon the location of the brewery. In addition, if the city uses multiple sources for their water, the source may be different from season to season. Of greater impact, however, is that the water obtained from municipalities is often treated to ensure that no harmful pathogens or ions exist. To ensure a safe water supply, most municipalities add chemicals.

Water purification often begins by adding compounds such as aluminum sulfate or iron(III) chloride. These compounds react with water to make aluminum hydroxide or iron(III) hydroxide. The hydroxide salts coagulate and entrap organic solids as they precipitate from the water. The sulfate and chloride ions that remain in the solution raise the overall concentration of these ions a little, but the removal of the suspended matter is more beneficial.

The purification plant then adds a disinfectant to the water to reduce or eliminate the presence of pathogenic organisms. This can be done by either adding chlorine gas (Cl_2) or sodium hypochlorite (NaOCl). In water, both are sources of the hypochlorite ion (OCl^-). These species are very powerful oxidizers and destroy the cell walls of the microorganisms. One problem exists with these disinfectants, though. They do persist in the water supply and can be found in measureable quantities in the brewery water. These oxidants can also cause damage to the malt if the water is used without removing them.

The other issue is the presence of byproducts that result from the disinfection process. These oxidizers can react with organic material in the water and form trihalomethanes and haloacetic acids. These compounds are potentially carcinogenic and chronic exposure to them causes other health issues. Their presence in the water is highly regulated by state and federal authorities. For the brewer, however, these compounds impart a taste to the finished beer that is perceived as an off flavor.

So, at the very least, they must be removed to protect the flavor of the beer. Their removal is accomplished by passing the water through a charcoal filter. The charcoal absorbs most organic compounds and the disinfection byproducts. It should be noted, however, that after passing the water through the charcoal filter, it has lost all of its disinfectant (i.e., bacteria can again grow in the water if there are any sources of contamination.)

CHECKPOINT 5.5
Use the information in this chapter to draw a diagram illustrating the hydrologic cycle.
What is the likely formula of the trihalomethane that results from the addition of chlorine gas (Cl_2) to water contaminated with organic matter?

5.4.2 What Makes up Water?

Water's chemical formula is H_2O. As we discovered in Chap. 2, water is a polar molecule that can dissolve other polar substances. Gases, such as CO_2 and O_2, tend not to be polar and as such, tend not to dissolve in water. Many of the larger organic molecules tend to be only sparingly soluble in water as well. On the other hand, ionic compounds have variable solubility. Some are quite soluble, and others are very insoluble.

5.4.2.1 Cations in Water

The typical ions that are found in drinking water include calcium (Ca^{2+}) and magnesium (Mg^{2+}). Both come from the dissolution of rocks that are permeable by water. Calcium and magnesium tend to occur together, with calcium as the major ion in water. Other ions are also possible.

Calcium and Magnesium Calcium and magnesium contribute to the hardness of the water sample. Two forms of hardness exist. *Temporary hardness* is the result of calcium and magnesium in the presence of carbonate or bicarbonate. If the water has temporary hardness, boiling it for a few minutes will reduce the level of dissolved calcium in the water as shown in Fig. 5.17.

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3\,(s) + H_2O + CO_2\,(g)$$

Fig. 5.17 Boiling water with temporary hardness reduces the calcium and magnesium content

Water with *permanent hardness* is the result of the presence of anions of sulfate, nitrate, chloride, and others. These anions do not form solids with calcium and magnesium when heated and instead remain in solution. This is somewhat desirable as both calcium and magnesium are both necessary at different stages of the brewing process. For example, flocculation of yeast during the cold crash stage of fermentation is sluggish when the calcium level is low in the water.

At nearly every concentration level, calcium tends to be beneficial. Too high of a level, however, can cause the formation of beer stone (calcium oxalate) on the vessels and kegs in the process. Magnesium acts very similarly to calcium, but at levels greater than about 15 ppm, can cause some issues. Above this concentration, a bitter taste becomes evident. In addition, digestive issues such as a laxative effect can be noted in those that consume this concentration.

Iron Iron ions can be found in some water supplies. Often these occur from poor plumbing systems (either in the municipality or within the brewery). If iron is found in the water, it can exist as one of two forms (Fe^{2+} and Fe^{3+}). The ferrous ion (Fe^{2+}) is typical in iron-containing waters that have not been aerated. Water that has been aerated typically contains the ferric ion (Fe^{3+}). When the levels of iron are high in water, rust stains appear on fixtures, the water takes on an orangish or rust-colored hue, and the flavor can be very metallic. But even low concentrations of iron above 0.5 ppm are harmful in the brewery. It is toxic to yeast at this level and causes any of the tannins in the beer to oxidize faster, imparting poor flavors to the resulting product.

Copper Copper ions can enter the water supply when they leach into ground water. Copper can also enter the water if the pH of the water supply is acidic and copper pipes are used. At levels greater than 10 ppm, copper can be toxic to yeast. In addition, it can speed the oxidation of tannins and cause permanent haze. Humans, on the other hand, can react to levels as low as 1.3 ppm. This can result in gastrointestinal distress or, in some cases, kidney or liver damage.

Sodium This ion enters the water stream naturally from surface and ground waters. It also gets into brewery water if the water used is conditioned using an ion-exchange conditioner. While moderate and low levels have a minor impact (high sodium levels can affect yeast growth), they do affect the flavor of the finished beer. At levels above 150 ppm, the beer will taste salty. At levels less than this, the sodium imparts a perceived sweetness to the beer.

Potassium This ion also arises in brewery water from natural sources. It has effects that are similar to sodium. High levels of this ion in beer can cause digestive problems. Very high levels can affect cardiovascular function in humans.

Other metal cations Many other metal cations may find their way into the water that the brewer uses. For example, if lead pipes are part of the supply of water to the brewery, it may be possible to have some lead dissolved in the water. Most of these cations are not desirable at anything more than trace levels, where they are useful for yeast health. Beyond those levels, they can be toxic to the yeast and even toxic to humans.

5.4.2.2 Anions in Water

The typical anions found in brewery water are carbonates and bicarbonates. These arise from natural sources and have effects on the brewing process, the health of the yeast, and on the flavor of the finished beer.

Bicarbonate and Carbonate As we will discover throughout this text, these ions are very important to the brewing process. They arise naturally in the water from its exposure to air (see Fig. 5.18). The result of dissolving carbon dioxide in water is the formation of carbonic acid. Carbonic acid then decomposes into the bicarbonate anion and a proton. The proton lowers the pH of the solution. The bicarbonate anion can further decompose into the carbonate anion and release another proton (and further lower the pH); however, this last reaction only occurs when the pH of the solution is already rather high.

Bicarbonate and carbonate anions can also be added to water through its contact with carbonate containing rocks, such as in carbonate aquifers. Figure 5.19 illustrates the reactions of the carbonate anion in water. The reaction of carbonate anions with water gives rise to the bicarbonate anion and an anion of hydroxide. The hydroxide results in the increase in the pH to more alkaline values.

Water that has been exposed to both carbonate containing rocks and air (containing carbon dioxide) has both carbonate and bicarbonate anions in it. In addition, these waters tend to have pH values that are greater than rainwater, but less than well water from a carbonate aquifer.

Chloride Chloride in the brewery water occurs naturally. At levels up to about 350 ppm, it can impart a beneficial effect on the fullness of the flavor of beer. At levels above 500 ppm, it can interfere with the flocculation of yeast.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

Fig. 5.18 Formation of bicarbonate and carbonate from dissolution of CO_2. The second reaction predominates in water. The third reaction occurs only in very alkaline (pH > 10) water

$$CaCO_3 \rightleftharpoons CO_3^{2-} + Ca^{2+}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

Fig. 5.19 Formation of bicarbonate resulting from the dissolution of carbonate containing rocks in water. Note that the reaction also generates hydroxide ions

Fluoride Many municipalities in the USA add fluoride to the drinking water and some natural deposits can increase the level of fluoride in ground waters. The addition of fluoride has been very useful in the prevention of dental caries (cavities) in both adults and children. The US Environmental Protection Agency (US EPA) maximum contaminant level for fluoride is 4.0 ppm. Consumption of water containing fluoride above this level can cause pain and tenderness in bones.

Nitrate and Nitrite These ions not only enter water naturally from deposits, but also can indicate contaminated water. In oxygenated water, the level of nitrite is usually quite low as it becomes oxidized to nitrate. The US EPA maximum contaminant level for nitrate is 10 ppm and for nitrite, it is 1 ppm. Water containing more than these levels causes blue baby syndrome in infants. Nitrite is toxic to yeast and both nitrite and nitrate can form carcinogenic compounds during the process to make beer. Whenever possible, water containing nitrates and/or nitrites should be avoided.

Sulfate Sulfate in brewery water can be a very useful anion. At low levels, it can be beneficial in creating a drier flavor. It can also help enhance the bitter hop flavor. At levels above about 250 ppm, it can begin to impart a slightly salty flavor. When those levels get above 400 ppm, the sulfate can cause gastrointestinal distress. The flavors of the traditional Pale Ales made in Burton-on-Trent, England, are considered well enhanced by the high levels of sulfate (>600 ppm) in the well water used. Note that this level is far above the concentration that might cause stomach issues. In the production of beer, the greatest impact is that it can be converted to SO_2 and H_2S by yeast or other microbes. These compounds can add poor off-flavors; H_2S smells like rotten eggs.

5.4.2.3 Residual Alkalinity

Residual alkalinity is a measure of the amount of basic ions that will impact the pH of water after all of the carbonate and bicarbonate have complexed with the available calcium and magnesium. For the brewer, residual alkalinity is a bad thing. Any of these anions that remain will increase the pH of the water. And when the brewer uses such water to mash, the pH of the system may cause the extraction of tannins from the grain.

Kolbach, in 1953, recognized that calcium and magnesium react with the alkalinity in water. On a per mass basis, 1.4 equivalents of calcium can react with 1.0 equivalent of alkalinity. In addition, 1.7 equivalents of magnesium can neutralize 1.0 equivalent of alkalinity. Thus, the residual alkalinity of a sample of water is:

$$\text{Residual Alkalinity}(\text{ppm}) = \text{Total Alkalinity (ppm)} - \left(\frac{\text{ppm Ca}}{1.4} + \frac{\text{ppm Mg}}{1.7}\right) \tag{5.1}$$

The residual alkalinity can be adjusted by addition of acid (to neutralize some of the total alkalinity). If such a method is used, the acid chosen should be neutral to the brewing process. Thus, the use of hydrochloric acid (HCl) is not a good choice. The use of phosphoric acid (H_3PO_4) is a more common choice. The phosphate ion is useful in the brewing process and is even produced naturally by the mashing of malt. Other ways to adjust the residual alkalinity include the addition of calcium and magnesium to the water. This would increase the amount of ions that can react with the total alkalinity.

Managing the residual alkalinity is very important in the brewing process. In addition to making sure that enough calcium and magnesium are present in the water to take care of all of the alkalinity, it is vital that additional calcium and magnesium remain. Those ions cause the isomerization of hop acids, aid in the flocculation of yeast, help form foams for the head, and the list goes on. If the water used is not treated or adjusted to reduce the residual alkalinity, the finished beer (and the overall brewing process) can suffer.

CHECKPOINT 5.6

Where does nitrate in ground water come from?

If a water sample has 200 ppm chloride, how many ppm sodium would it have? (assume that the only cation in the water is sodium).

How would adding more calcium reduce the residual alkalinity of a water sample?

Chapter Summary

Section 5.1

The barley plant is a member of the grass family.

Barley is dried to about 12 % moisture before being sent to the malthouse.

Sorting and grading provide information about the quality of a barley harvest.

Section 5.2

The barley seed germinates when water rehydrates the corn.

Gibberellic acid triggers the production of enzymes that convert the endosperm into usable sugars.

The process of malting includes steeping, germinating, and kilning.

Section 5.3

Maillard reactions are complex but involve three main steps.
The products of the reactions increase the color of the malt and impart caramel, toasty, malty, or burned flavors to the malt.

Section 5.4

Water is the most important ingredient in the brewhouse.
The makeup of cations and anions in the water is a result of the source of the water and any added contamination.
Residual alkalinity must be managed to avoid extraction of tannins and to ensure the adequate concentration of calcium and magnesium during the brewing processes.

Questions to Consider

1. Why is water considered the most important ingredient?
2. Use the Internet to look up reasons why some believe that barley was likely one of the first grains grown.
3. If a barley corn's husk is damaged, will this change how the seed hydrates?
4. To take question #3 further, assume that the damage to the barley corn is a hole through the husk, pericarp, and testa. Will this change how the seed hydrates?
5. Use the Internet and identify countries in Europe that produce barley.
6. Use the Internet to visit the American Malting Barley Association website. Which cultivars are recommended for next years' crop?
7. What is the minimum mass of a bushel of Grade 1 2-row malting barley?
8. Why is the air on during kilning slowly ramped up, rather than being set at the initially warm temperature?
9. One of the compounds produced during the initial stages of the Maillard Reaction is diacetyl. Why does the flavor of this compound decline as the malt is further kilned?
10. A water sample is reported to have a total alkalinity of 100 ppm as $CaCO_3$. If the sample contains 50 ppm Ca and 12 ppm Mg, what is the residual alkalinity of the sample?
11. What is the benefit to the malt in a floor maltings? What are the disadvantages for this method of preparing malt?
12. Use the Internet to look up how your city or town gets its water. How is it treated prior to being delivered to your home?
13. What is the likely fate of the roots that grow on the barley seed as it is modified?
14. Would sulfuric acid be a good choice to decrease the alkalinity of a water sample that was to be used in the brewhouse? Why or why not?
15. Can wheat, another member of the grass family, be malted? Why or why not?

16. What would a brewer need to do to use rainwater as the water in the brewhouse?
17. Why is rainwater typically acidic, but well water from a carbonate aquifer typically alkaline?
18. Rank the pH values of water from a carbonate-sandstone aquifer, surface water, and rainwater.
19. What would you predict to be the effect of adding gibberellic acid to a sample of barley that is about to become malted?
20. Estimate the total time to convert a bag of barley that has been freshly harvested into a bag of malt that is ready to be used by the brewer.
21. How many milligrams of calcium (as calcium carbonate) are there in 1.0 bbl of water with 50 ppm calcium (as calcium carbonate)?
22. If a 1.0 bbl water sample has 80 ppm total alkalinity, 50 ppm calcium, and 10 ppm magnesium, how many milligrams of calcium (as calcium carbonate) must be added to give a residual alkalinity of 0.0 ppm.

Laboratory Exercises

Germination of Barley

This experiment is designed to allow you to see the changes that barley seeds undergo during the germination process. The entire experiment takes 3–7 days to complete, but analysis of the seeds along the way is very helpful in learning the key names of the parts of the seed as well as observing the growth of the seeds.

Equipment Needed

Barley—seeds that are ready for planting
Magnifying glass
Paper towels
100 mL beaker
water

Experiment

Each student group should obtain 20–30 barley seeds for this experiment. The seeds are placed into the beaker and then room temperature water is added. The seeds are gently stirred and left to sit in the water for an hour. The water is then removed by decanting it from the seeds. Then, slightly warm water is added to cover the seeds. The seeds are again stirred and left to sit for another hour. Then the water is decanted and the seeds placed onto a paper towel that is wet with water.

The paper towel is folded over and water is added to wet the towel completely. The paper towels are placed in a cool dark place (such as a drawer) and left until the next day. Periodically over the next 7 days, the paper towel is observed. It should remain damp during the entire period.

Observations should be recorded and, using a magnifying glass, drawings of the seeds should be made. At each observation, one of the seeds should be pulled apart (if possible) and the interior of the seed drawn.
Make a table containing the following headers:

- Time since first steeped
- Total Number of seeds
- Number of seeds that have chitted
- Number of seeds with roots that are 10 mm long
- Number of seeds with acrospire that is visible.

Plots of the data in the table can be used (time versus percent that…) to graphically observe the same data.